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# The beryllium content of igneous rocks

E. B. SANDELL

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*(Received 3 Decembre 1951)*

ABSTRACT

On the average, granitic rocks contain about 3 p.p.m. of Be and rocks of basaltic composition a little less than 1 p.p.m. If silicic and subsilicic rocks are weighted equally, an average value of 2 p.p.m. or less may be assigned as the Be content of the upper lithosphere.

GOLDSCHMIDT and PETERS [6] have presented a broad outline of the geochemistry of beryllium. They showed that beryllium is more abundant in silicic than in subsilicic rocks, and that it is concentrated even more strongly in alkalic rocks such as nepheline syenites. This distribution is in accord with the small ionic radius of beryllium (0·34 Å) and its low charge, which lead to its enrichment in late crystallizates. It is believed by these authors that beryllium replaces silicon (0·39 Å) in the lattice of silicates. Two values for the abundance of beryllium in the lithosphere were reported by GOLDSCHMIDT and coworkers at different times. The first [6], based principally on the determination of the element in German granites and gabbros, is approximately 2 p.p.m. (parts per million or grams per ton) of Be (or 5 p.p.m. of BeO). The second [5], based on the content of a composite of shales, is 6 p.p.m. Be (15 p.p.m. BeO). The latter figure was preferred by GOLDSCHMIDT, as shown by the fact that he used this value in his compilation of the abundance of the elements [4]. SANDELL and GOLDICH [14] reported an average of 7 p.p.m. Be in 9 American silicic samples, 5 of which were from the Llano region of Texas, and one a composite of 5 Minnesota granitic rocks. SAHAMA [9] has determined beryllium in a number of Finnish rocks, and LANDERGREN [7] has studied its occurrence in Swedish iron ores and the rocks associated with them.

Further investigation of the abundance of beryllium seemed desirable because of the relatively small number of samples analyzed so far and the rather approximate values furnished by the spectrographic methods hitherto applied. Accordingly, the beryllium content of a number of igneous rock composites, prepared on the basis of silica percentage, has been determined. (These composites have been used previously in a study of the abundance of gallium [12]. They were prepared by taking equal weights of the individual rocks.) The determination was made by an improved fluorimetric method [13], in which morin is used as reagent after separation of beryllium from such elements as iron, magnesium, and calcium. This method permits the detection of approximately 0·2 p.p.m. Be in a 0·1 g sample. The fluorescence intensities of sample and standard solutions were compared visually.

The results obtained in the analysis of the composites are given in Table 1 and of some miscellaneous samples in Table 2. The experimental values have been increased by 10% to correct for the small loss of beryllium that usually occurs in the separation.

*Table 1. Beryllium in composites of igneous rocks*

| *Silica range* % $SiO_2$ | *Average silica* % $SiO_2$ | *Rock type and number of samples* | *Region* | *Beryllium content p.p.m.* Be |
|---|---|---|---|---|
| 80·6–76·3 | 77·7 | Granite (12) | U.S.A. | 3·0, 3·1 |
| 81·5–75·1 | 77·0 | Granite (8) | U.S.A. and Canada | 3·0 |
| 77·4–71·5 | 74·1 | Granite, etc. (9)[1] | California | 2·4 |
| 76·8–68·2 | 73·1 | Granite (5)[2] | Texas (Llano region) | 5·5 |
| 74·3–70·6 | 72·6 | Granite (7) | Canada | 2·4 |
| 73·9–70·0 | 72·0 | Granite (9) | Africa | 3·3 |
| 69·6–65·5 | 68·4 | Granite, etc. (14)[3] | U.S.A. and Canada[4] | 2·7 |
| — | — | Granitic[6] | Minnesota | 3[5] |
| 65·7–52·7 | 62·0 | Diorite (7) | Oregon and California | 1·6 |
| 57·7–44·4 | 50·0 | Sub-silicic (24)[6] | Various[7] | 0·9, 0·8 |
| 50·1–47·4 | 48·6 | Basalt | Michigan[8] | 0·9 |
| 50·4–46·0 | 47·4 | Basalt | Michigan[9] | 0·9 |
| 54·7–33·4 | 42·8 | Ultra-basic (6)[10] | —[11] | $<$0·25 |
| 53·2–48·3 | 50·7 | Anorthosite (3) | New York, Minnesota and Montana | $<$0·5 |
| 64·1–56·0 | 60·3 | Syenite (6) | New York and Minnesota | 2·2 |
| 57·9–49·6 | 53·1 | Phonolite (4) | Africa | 7 |

[1] 4 granites, 2 quartz monzonites, 1 monzonite, 2 granodiorites.

[2] For petrographic description and analyses see reference [2].

[3] 6 granites, 1 granite porphyry, 1 felsite porphyry, 1 porphyry, 1 quartz monzonite, 1 granodiorite, 1 diorite, 2 dacites.

[4] Canada 2, New York 1, Texas 2, Montana 2, Wyoming 1, California 2, 4 from unspecified U.S. or Canadian localities.

[5] From earlier analyses [14].

[6] 9 gabbros, 1 norite, 4 diabases, 8 basalts, 1 peridotite, 1 pyroxenite.

[7] Eastern and western U.S. 13, New Foundland 1, Africa 1, Antarctica 3, India 1, unspecified localities (probably U.S.) 5.

[8] Weighted composite of the Greenstone flow [1].

[9] Weighted composite of Kearsarge flow [1].

[10] 1 peridotite, 1 dunite, 1 harzburgite, 1 bronzitite, 1 pyroxenite.

[11] New Foundland 3, U.S. 2.

## Discussion of Results

The average beryllium content of 7 granitic composites (a total of 64 individual rocks) whose average silica content ranges from 68 to 78% is 3·2 p.p.m. If the small central Texas composite, whose beryllium content is about double that of the others, is omitted, the average is 2·8 p.p.m. We will take 3 p.p.m. as the average for granites and related rocks. There is no marked variation in the beryllium content of the granitic composites with variation of silica content. Experimental error may explain this in part, *i.e.*, the error in determining 3 p.p.m. Be could well be $\pm$0·3 p.p.m. ($\pm$10%).

The average for rocks of basaltic composition (47 to 50% silica) is 1 p.p.m. or a trifle less. Accordingly the common mafic rocks contain about one-third as much beryllium as the granitic rocks. A composite of diorites gave a value, 1·6 p.p.m. Be, falling between the granites and basaltic rocks. A small composite of ultrabasic rocks contained no detectable beryllium, *i.e.*, less than 0·2 or 0·3 p.p.m. For rocks of the main sequence the beryllium content is thus clearly a function of the silica content.

*Table 2. Beryllium in miscellaneous samples*

| | *p.p.m.* Be |
|---|---|
| Obsidian, Obsidian Cliff, Yellowstone Park[1] | 5·5 |
| Quartz monzonite, Rockville, Minnesota[2] | 2·0 |
| Biotite from Rockville, Minnesota, quartz monzonite | 0·5 |
| Microcline from Rockville quartz monzonite | 1 |
| Plagioclase (An = 28) from Rockville quartz monzonite | 4 |
| Quartz from Rockville quartz monzonite | <0·25 |
| Granite, Devil's Slide, Percy quadrangle, N. H.[3] | 3·3 |
| Amphibole from Devil's Slide granite[3] | 26 |
| Diabase, harbor, Grand Marais, Minnesota[4] | 1·7 |
| Diabase, Lake Co., Minnesota[5] | 1 |

[1] Goldschmidt and Peters [6] report 0·01% BeO, or approximately 35 p.p.m. Be, in an obsidian from this locality.

[2] For petrographic description see Tatge [15] and Woyski [18].

[3] For bulk analysis see [14], p. 114.

[4] For bulk analysis see [14], p. 110.

[5] For description and bulk analysis see [3].

From the results of the analyses of the composites a value may be derived for the beryllium content of the upper lithosphere. Such a figure must be approximate at best because the "upper lithosphere" is not well defined and its quantitative rock composition is not well established. Nevertheless, such an average, even though it lacks an exact significance, has some value, particularly from the comparative standpoint. For the present purpose, granitic rocks and the common mafic rocks will be weighted equally. An average value of 2 p.p.m. or slightly less in thus obtained. This figure is to be looked upon as more or less tentative, in part because the number of samples from which it is derived is still quite small. If the rocks examined can be considered reasonably representative it seems unlikely that the average will fall outside the limits 1 and 3 p.p.m.

Because the average given by the composite of the five Llano rocks of central Texas is so much higher than that of similar rocks, four of these rocks were re-analyzed individually by the improved fluorimetric method for beryllium. The new values are given below with the old values [14], obtained by a somewhat less exact method [11], for comparison:

| | *New value* *p.p.m.* Be | *Old value* *(1943)* *p.p.m.* Be |
|---|---|---|
| Llanite | 6 | 14 |
| Granite, Bear Mtn. | 8 | 10 |
| Granite, Granite Mtn. | 7 | 8 |
| Granite, Cassaday | 4 | 5 |
| Quartz monzonite, Town Mtn. | — | 3 |

The agreement is moderately good except for llanite. The difference between the new and the old values is too large to be attributed to analytical error. Contamination

or some heterogeneity in the sample are possible causes for the discrepancy. The mean of the individual new analyses agrees with the value obtained by analysis of the composite. From the result obtained with the Llano composite, compared to other granites, it appears that rocks of similar bulk composition can show appreciable differences in their beryllium content. Examination of a larger number of composites than attempted here will be necessary to establish the degree of uniformity in the distribution of beryllium in similar rocks.

The average of 2 p.p.m. of beryllium for igneous rocks arrived at above is in agreement with GOLDSCHMIDTs first estimate [6]. His later estimate [5], based on the sedimentary abundance of the element, seems to be too high. The present results are somewhat comparable to those of SAHAMA [9] for rocks of southern Lapland. He found no detectable beryllium in ultrabasic rocks or gabbros and dolerites and only about 1 p.p.m. in granites. Considering that the spectrographic method used by SAHAMA is less sensitive than the fluorimetric method, and that the former gives results correct only by a factor of two or three, our values are not inconsistent. In a composite sample of 54 East Fennoscandian rapakivi granites, SAHAMA [10] found 0·001 % BeO or about 4 p.p.m. of Be, again a value in accord with the present findings. LANDERGREN [7] reports that the beryllium content of the rocks associated with iron ores of central Sweden is usually below the limit of spectrographic detectability (0·001 % Be).

It appears that beryllium is definitely less abundant than lithium in the upper lithosphere and possibly less so than boron (WASSERSTEIN [16]).

A large fraction of the beryllium in igneous rocks doubtless occurs in the feldspars. The component minerals of the coarse-grained Rockville, Minnesota, quartz monzonite were separated and beryllium determined in each (Table 2). It is interesting that 4 p.p.m. Be was found in the plagioclase (An = 28) but only 1 p.p.m. in the microcline. Approximately 0·5 p.p.m. was present in the biotite (including zircon and apatite). No beryllium was found in the quartz. The two feldspars are present in approximately equal amounts in this rock and comprise roughly three-fourths of the whole; biotite makes up about 8 % of the rock.

The alkalic amphibole separated from a New Hampshire granite (3·3 p.p.m. Be) was found to contain 26 p.p.m. Be. The amphibole is estimated to make up 5 % of the rock, and therefore accounts for about one-third of the total beryllium, the remainder presumably being contributed by the feldspar.

The cosmic abundance of beryllium is of special interest because it is believed that its deficiency (like that of lithium and boron) compared to other elements of low atomic weight is the result of the disintegration of the beryllium atom by proton bombardment at high temperatures and pressures. GOLDSCHMIDT regarded 1 p.p.m. as the most probable value for the abundance of beryllium in silicate meteorites, the figure being derived from his own results and those of the NODDACKS [4]. Since it has been found that rocks of basaltic composition contain about 1 p.p.m. of beryllium it would be expected that silicate meteorites would contain less on the average. Further investigation of the beryllium content of meteorites appears desirable.

*Manner of occurrence of beryllium in igneous rocks*—At the present time this is largely a matter of conjecture. As already noted, there are reasons for believing that

beryllium may replace silicon in the lattice of rock-forming minerals. An argument against such substitution may be based on the occurrence of the two elements independently of each other in most silicate minerals in which beryllium is a principal constituent, *e.g.*, beryl and helvite. However, the replacement of silicon by beryllium in a lattice is not entirely unknown. F. MACHATSCHKI ([6], p. 370) has shown that this substitution takes place in a beryllium-bearing titanian clinohumite. Moreover, only a very limited replacement of Si by Be is required for the case of the rock-forming silicates. If it is supposed that this substitution does take place, the excess of two negative charges resulting can be compensated by the introduction of a trivalent cation in place of a univalent cation in the mineral. For example, RANKAMA and SAHAMA [8] explain the presence of lanthanum in potassium feldspars by the simultaneous substitution of La for K and Be for Si. The absence of beryllium from quartz (Rockville quartz monzonite, Table 2) may be a consequence of the difficulty of compensating the excess negative charge produced if beryllium should tend to replace silicon.

Replacement of aluminium by beryllium in a lattice may be considered a possibility, although the radii of the two are quite different ($Be^{+2}$ 0·34, $Al^{+3}$ 0·57 Å). If this substitution should take place readily the distribution of beryllium in igneous rocks should resemble that of gallium, which without doubt replaces aluminium in silicates. Actually there is little resemblance between the behaviour of the two. It may be noted that the beryllium content of a composite of anorthosites ($Al_2O_3$ = 28%) is less than 0·5 p.p.m. In more silicic rocks, replacement of Al by Be might conceivably come more to the fore. WICKMAN [17] has suggested a substitution of the type $CaAl_2Si_2O_8$–$Y(BeAl)Si_2O_8$ in low temperature feldspars. A test of such substitutions should be possible by accurate determination of the rare earths and other trace elements in feldspars. If the rare earths actually play the role they are thought to play in connection with beryllium in feldspars, there should be a large difference between the rare earth contents of the potassium feldspar and plagioclase of the Rockville quartz monzonite (Table 2).

Finally, it may be postulated that beryllium does not replace any cation in silicate minerals but crystallizes as an independent beryllium mineral, especially in late differentiates in which it has accumulated. The low concentration of beryllium in the melt would seem to make it difficult for an independent beryllium mineral to form; a very small "solubility" of the mineral would be implied. The presence of significant quantities of beryllium in aqueous inclusions is improbable. In some rocks, certain accessory minerals, *e.g.*, allanite, might contribute some beryllium.

The occurrence of beryllium in igneous rocks by ionic replacement appears the most probable mode. Much detailed work will be required to trace the distribution of the element in rock series and among the minerals of a given rock.

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# Sur la météorite d'Oubari

E. Jérémine et M. Lelubre

*(Received 26 November 1951)*

ABSTRACT

The meteorite found on September 27th, 1944 in the erg (sandy desert) of Oubari (Fezzan, Eastern Sahara) is a brecciated pyroxene peridotite chondrite. Although intensely crushed it contains fragments which show the unaltered primary structure of the stone: coarse crystals of hypersthene which irregularly lump together olivine, diopside, and clinopyroxenes-features (poikilitic structure) in which it resembles certain terrestrial rocks.

The chemical composition is near to that of the amphoterite of Jelica.

Cette météorite a été trouvée par l'un des nous (M.L.) le 27 septembre 1944 dans l'erg d'Oubari (Fezzan, Sahara Oriental) à 2 km environ du village de Gabr'on (26° 48′ lat. Nord, 13° 35′ long. Est). On n'a pu obtenir aucun renseignement sur la date ou les conditions de la chute. Rappelons que le Fezzan forme une vaste cuvette au Nord des deux massifs cristallins du Hoggar et du Tibesti.

La pierre a été envoyée en 1945 à A. Lacroix qui a fait exécuter son analyse chimique par le Laboratoire d'analyse de roches du Centre National de la Recherche scientifique et en a commencé l'étude un peu avant sa mort, mais n'a laissé aucune observation rédigée.

La météorite gisait dans les contreforts Ouest de la grande dune de Gabr'on, sur le flanc nord, le plus raide, à peu près à mi-pente. Les fragments étaient dispersés sur une espace sensiblement elliptique, dont le grand axe, orienté approximativement EW, mesurait environ 5 m et le petit axe 3 m. Aucun fragment n'a été observé plus bas dans le creux de la dune. Les plus gros fragments (dont un de 15 cm) se trouvaient vers le milieu, et les petits débris et la poussière ont été dispersés aux extrémités de l'ellipse. Les fragments ont été posés sur le sable, attirant l'attention par leur couleur noir de poix; aucun n'a été enfoui dans le sable, ce qui montre que la météorite ne s'est guère enfoncée lors de la chute; en touchant le sol, elle s'est brisée en quelques gros blocs et en multiples petits morceaux.

On a recueilli la quasi totalité des fragments de la pierre qui devait peser un peu plus de 8 kg. Le plus gros atteint le poids de 2 kg 156. Les essais de reconstitution ont montré que la météorite, d'une forme irrégulière, grossièrement pyramidale et allongée mesurait $20 \times 15$ cm dans la plus grande dimension. Les trois faces partant du sommet du grand fragment (Fig. 1 et 2) présentent de rares piézoglyptes, généralement peu profonds, soit larges et irréguliers, soit petits, circulaires. La surface de ces faces est recouverte d'une mince croûte noire qui ne dépasse pas 1 mm et s'amincit jusqu'à 0·2–0·1 mm; elle est lisse mais craquelée en un système de fissures réticulées dont la maille mesure de 2 à 5 mm; cette fissuration est probablement due aux actions désertiques. Dans les parties apparemment préservées de l'érosion, la surface est terne, finement granuleuse. Les cassures des morceaux brisés se présentent sous deux aspects différents; fraiches, elles sont assez régulières, mais celles qui ont sejourné dans le sable ou surtout celles qui ont été exposées

à l'action érosive du sable et du vent, sont extrêmement rugueuses, parsemées de creux profonds et de saillies pointues. Ces saillies portent en leur sommet soit

Fig. 1. La météorite vue au-dessus du sommet réunissant les trois faces. Piézoglyptes au Nord du sommet.

des chondres, plus résistants en raison de leur structure, soit de grains de fer, généralement mats et bruns, parfois à éclat métallique. Dans les cassures apparaissent

Fig. 2. Fissures réticulées de la surface.

de grosses taches brunes our rousses, aux contours très découpés au milieu desquelles on aperçoit parfois un grain métallique. Les parties qui ont été exposées

à l'érosion désertique sont légérement vernissées et les saillies sont devenues faiblement brillantes. Les chondres, atteignant 1 mm de diamètre, sont bien visibles dans les deux cas. Parfaitement sphériques, gris, ils sont encastrés dans une fine masse grenue, claire, presque blanche. Dans la profondeur des creux apparaissent parfois nettement des grains colorés en vert-pomme. L'étude de la poudre de ces grains a montré qu'ils sont constitués par de l'olivine.

Un caractère très spécial de cette météorite est sa richesse en gros (jusqu'à 2 cm) et petits (2 mm) fragments anguleux, noirs, mats, à surface inégale. Un

Fig. 3. Surface polie montrant la distribution de minéraux métalliques et la structure bréchiforme de la pierre. Gross. 2.

échantillon poli pour l'étude en lumière réfléchie, fait ressortir avec netteté ces fragments noirs (Fig. 3). Quant aux taches brunes, dont il a été question plus haut, elles sont dues probablement à une oxydation locale dans un milieu humide; leur configuration sinueuse rappelant l'écoulement d'une goutte liquide, est soulignée par un mince filet extérieur plus foncé. Les éléments métalliques sont très irrégulièrement répartis: en grains de 2 mm en moyenne, en filonnets de 3–5 mm et enfin, en granules et poussière de toutes dimensions.

## Description Pétrographique

### *1. Composition minéralogique*

L'étude au microscope polarisant montre la présence des minéraux habituels des chondrites: péridot, ortho-mono et clino-pyroxènes, peu de feldspaths, quelques grains et cristaux de merrillite et comme exception de l'oldhamite. La partie métallique est représentée par le fer nickelé et la troïlite. Les minéraux essentiels—

péridot et pyroxènes, sont de taille très variable (les grands ne dépassent pas quelques mm, les plus fréquents sont de 0·3 mm), le broyage les réduisant peu à peu en poussière.

Le *péridot*, en cristaux réguliers, isolés ou en amas de grains et granules ou, enfin, comme élément des chondres, est très abondant. Les cristaux sont fissurés et les fissures souvent remplies de matière vitreuse riche en poussière métallique. Par la recherche des bissectrices et par la mesure avec la P.F.*, on peut constater que l'angle 2 V est plus petit que 90° et que le signe optique est négatif. Une forte dispersion empêche des mesures très précises. Le calcul d'après l'analyse chimique indique que ce péridot est plus riche en magnésie qu'en fer ($Mg_2SiO_4 = 35{\cdot}14$; $Fe_2SiO_4 = 22{\cdot}14$).

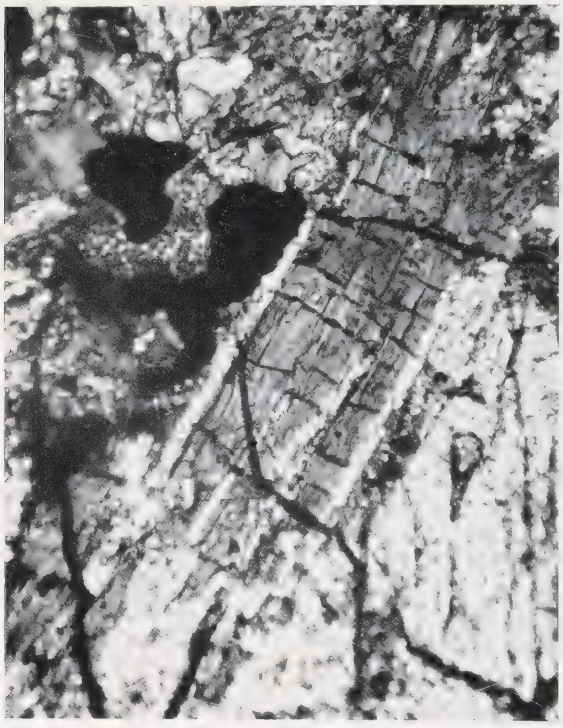

Fig. 4. Microphotographie d'une baguette d'hypersthène bordée de diopside. N+ Gross. 200.

Les *pyroxènes*, moins abondants que le péridot, appartiennent à des types très variés. Le *diopside* a pu être déterminé avec assez de précision dans les sections sans formes propres, incluses dans un grand cristal d'hypersthène et orientées presque parallèlement au plan des axes. Les deux indices de réfraction sont plus grands que ceux de l'hypersthène. L'angle d'extinction $n_g : c = 40°$ par rapport aux clivages très grossiers qu'il ne faut pas confondre avec des stries très fines d'une biréfringence faible, inclinées de 24° par rapport à $n_p$, appartenant probablement à un clinopyroxène. Le diopside se rencontre en outre en mince bordure autour des cristaux allongés d'hypersthène (Fig. 4). Sa haute biréfringence et son angle d'extinction par rapport à l'allongement permettent de le distinguer des clinopyroxènes. L'angle 2 V n'est pas grand.

Parmi les autres pyroxènes, l'*hypersthène* est le plus fréquent. Il forme des baguettes allongées, parfois assez grandes, isolées ou englobant les autres minéraux (Fig. 5), il entre aussi dans la constitution des chondres. Le plan des axes est parallèle à l'allongement, l'angle d'extinction égal à 0° et la biréfringence faible. L'angle 2 V déterminé par la P.F. n'a pas la même valeur sur des différentes sections. Le plus fréquemment il est égal à 76° (mesuré par ex. sur l'un des cristaux englobant poecilitiquement l'olivine). On a obtenu aussi 72°, 68°, 62° autour de $n_p$. Larsen donne pour l'hypersthène les angles 2 V: 63°, 75°, 81° et 90°. Enfin, l'un des

* P.F. = abréviation pour la "platine de Fedoroff."

pyroxènes, nettement orthorhombique, ayant l'angle 2 V = 88° appartient à un hypersthène très magnésien ou à une bronzite. (Sans correction par rapport à la différence entre les indices de la demi-boule = 1·649 et ceux du minéral qui sont inconnus.)

La *clinoenstatite*, moins répandue que l'hypersthène, se reconnait par ses fines macles répétées suivant $h^1$. Ces macles rendent difficile l'étude au microscope ou à l'aide de la P.F. On les voit dans les sections perpendiculaires à la bissectrice obtuse $n_p$. Le plan des axes est transversal à l'allongement. La bissectrice aiguë positive ($n_g$) se trouve dans les sections avec deux clivages où les macles apparaissent d'une façon très floue. L'extinction est de 36°. L'angle 2 V mesuré avec la P.F. ne dépasse pas 80°+. On peut rencontrer la clinoenstatite en bordure autour de l'hypersthène.

Les *plagioclases* donnent l'impression d'avoir cristallisé en dernier lieu. Ils occupent les interstices dans les chondres ou imprègnent suivant les fissures les

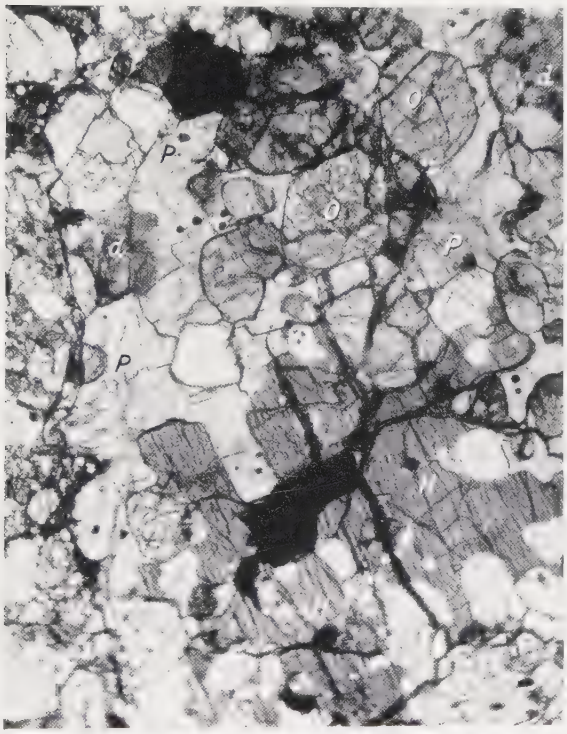


Fig. 5. Une portion du cristal unique d'hypersthène (*H*) englobant poecilitiquement l'olivine (*O*), le diopside (*d*) et pénétré par le plagioclase (*P*). N+ Gross. 90.

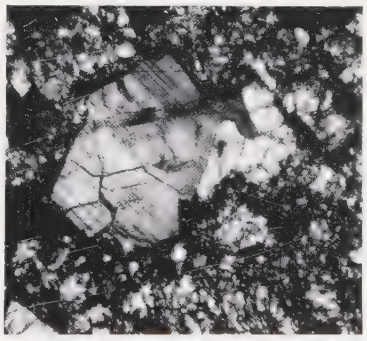

Fig. 6. Plagioclase maclé. On voit un petit pédoncule (en bas) englobé par l'olivine. N+ Gross. 90.

minéraux ferromagnésiens en les corrodant. La photographie (Fig. 6) montre un plagioclase maclé faisant partie d'un complexe car il est enveloppé partiellement par de l'olivine. Rarement visibles au microscope, les macles sont faciles à observer avec la P. F. Un plagioclase qui remplit les fissures dans un cristal poecilitique d'hypersthène, non maclé, perpendiculaire à la bissectrice $n_g$ avec un clivage net a donné: l'angle d'extinction de 6° et les indices $n_m$ et $n_p$ voisins du baume de Canada, donc un oligoclase à 20% d'anorthite. Mais quelques mesures sur d'autres sections avec la P.F. ont montré la macle de péricline et l'angle 2 V = 72° c'est à dire l'andésine à 30% d'anorthite. La même projection peut être interprétée comme la macle de l'albite = andésine à 32%. Par le calcul d'après l'analyse chimique suivant la méthode de A. Lacroix, on obtient un plagioclase à 26% d'anorthite. Pour expliquer ces contradictions il faut prendre en considération que les feldspaths des

météorites appartiennent aux variétés formées à haute température. Or, des récentes études [11] ont établi que les propriétés optiques de l'albite synthétique formée à haute température sont différentes de celles que possède l'albite pure des pegmatites et des granites (formée à basse température) et se rapprochent de celles des feldspaths sodiques des laves. Notamment, les extinctions sur la face $g^1$ (010), les angles 2 V, les indices de réfraction sont plus petits. Les différences diminuent à mesure que le plagioclase s'enrichit en anorthite. Les formes à haute température sont en outre probablement parfaitement miscibles avec le feldspath potassique. Il nous semble donc admissible que le plagioclase, de cette chondrite soit voisin de l'andésine à 30 % d'an. Il suffit, en effet, de 2 molécules d'$Al_2O_3$ supplémentaires dans l'analyse chimique pour obtenir ce plagioclase par le calcul.

Dans les sections minces qui traversent la croûte extérieure noire et opaque, la zone voisine de cette croûte est transparente et contient un élément isotrope incolore, à indice de réfraction faible dont la forme irrégulière rappelle celle des feldspaths. Il se trouve également dans les fragments noirs riches en matière fondue. Nous l'attribuons à la *maskélynite*.

La *merrillite*, en grains sans formes ou vaguement arrondis, moins réfringente que les minéraux ferro-magnésiens de l'entourage, montre de bons clivages dans deux directions et renferme en abondance des inclusions, surtout métalliques. Elle se présente parfois en amas de petits grains, légèrement déplacés les uns par rapport aux autres (résultat d'un écrasement). La biréfringence est faible, le signe optique négatif.

L'*oldhamite*, assez abondante dans l'aubrite de Bustee (achondrite à enstatite), dans les chondrites à enstatite de Hvittis et de Daniel's Kuil, est rare dans les autres chondrites (A. Lacroix a fait remarquer dans ses notes manuscrites que l'oldhamite est constante dans les météorites dépourvues de silicates ferrugineux). Nous l'avons aperçue dans un chondre complexe, composé d'olivine, de pyroxènes et de feldspath. Son indice de réfraction est plus fort que celui du péridot et des pyroxènes, l'isotropie est parfaite. Elle a plus d'analogie avec oldhamite de Hvittis que de Bustee, étant presque incolore. Mais dans un grain isolé d'une autre plaque mince, le minéral est légèrement teinté de rose.

### 2. *Structure*

L'apparence nettement bréchiforme de la structure, est encore plus accentuée en plaques minces. Les minéraux sont en fragments de taille variable, les cristaux isolés, limités cristallographiquement sont rares, ils se rencontrent surtout dans les chondres ou sont englobées dans les plages d'hypersthène. A côté des fragments de minéraux et de chondres, il existe des *débris* de *roches*. On les voit à l'oeil nu sous forme de morceaux anguleux, soit noirs, soit clairs.

Fragments *clairs*: les plus remarquables et bien caractéristiques pour la météorite d'Oubari sont composés d'une accumulation de plusieurs cristaux d'hypersthène atteignant 5 mm de diamètre, séparés les uns des autres par un amas désordonné de petits éléments de la pierre, y compris les débris des chondres. Chaque cristal d'hypersthène d'une orientation optique uniforme englobe poecilitiquement des minéraux variés. La Fig. 5 représente une partie d'un tel cristal enveloppant l'olivine en cristaux automorphes ou arrondis disséminés sans aucun ordre; diopside, ni automorphe, ni orienté par rapport à son hôte, bien que tous les deux parallèles au

plan des axes; rarement clinoenstatite; grains d'un minéral métallique. Cet hypersthène est en outre parcouru par un réseau de fissures, assez larges, remplies par le plagioclase dont il a été question plus haut (p. 221), présentant un faible décalage optique dans les différentes parties du cristal de l'hypersthène. Cette structure élégante est identique à celle de certaines roches terrestres (hypersthénite à olivine ou péridotite à hypersthène). Parfois l'hypersthène n'englobe que de l'olivine mais le plagioclase remplit toujours des fentes. Ces roches en miniature sont selon toute probabilité des résidus de la structure primaire de la météorite, échappés à la destruction par les actions d'écrasement, de thermométamorphisme et de recristallisation.

Dans d'autres cas les portions claires sont constituées par un agrégat de grains fins d'olivine, de plagioclase et de pyroxènes, montrant un cas classique d'écrasement par frottement et choc sans étirement. Cette structure est décrite par W. Wahl [12] dans la météorite de Varpaisjärvi (Finlande) sous le nom de "pavement structure" (en pavé). Il l'attribue à la recristallisation par le thermométamorphisme de la structure primitivement tuffacée.

Les chondres et les fragments des chondres dépourvus également du métal, appartiennent aussi aux portions claires de la météorite.

Fragments *noirs* ou *sombres*. Noirs et mats ou gris à l'oeil nu, ils montrent en sections minces un réseau plus ou moins dense de veinules noires irrégulières, entourant des cristaux arrondis ou sans formes propres d'olivine, rarement de clinoenstatite avec ses macles polysynthétiques. Le feldspath ne se voit plus que sous sa forme isotrope-la maskélynite. Ce phénomène commence par une désagrégation des minéraux en amas de très petits éléments autour des bords des cristaux et des bords des fissures qui les traversent. Si la clinoenstatite est bordée par du diopside c'est ce dernier qui est broyé. Une comparaison avec la cataclase de roches terrestres vient immédiatement à l'ésprit, elle peut être partielle ou complète. Dans le stade suivant la fusion de ces agrégats produit une matière vitreuse, soit brune et transparente, soit semiopaque (il suffit d'employer un fort grossissement et un bon éclairage pour le voir), obscurcie par des ponctuations métalliques. Légèrement translucide, elle permet de distinguer des silhouettes confuses des minéraux. Comme suite d'une fusion plus avancée, les veinules presque opaques apparaissent ternes en lumière refléchie à part quelques granules métalliques. On peut établir la résistence relative des minéraux à l'action calorifique: le plagioclase acide de cette météorite fond le premier, ensuite viennent l'hypersthène et le diopside, tandis que la clinoenstatite reste partiellement intacte, bien que ses macles sont brisées transversalement et enfin, l'olivine dont le point de fusibilité est le plus élevé, ressort nettement avec sa haute biréfringence et les formes cristallographiques à peine émoussées au milieu du réseau des veinules. L'origine calorifique des veinules parait évidente. Quant à la cause de l'élevation de la température nécessaire pour la fusion des minéraux, il faut la chercher dans la cataclase et les actions dynamiques. Comme exemple des phénomènes identiques dans les roches terrestres il suffit de citer les études de Shand [7], de Hall et Molengraaff [1] sur le massif de Vredefort (Transvaal). Ce massif qui comprend un ensemble de roches sédimentaires et éruptives (granites et syénites néphéliniques) a subi de très forts écrasements, les roches ont pris par places un aspect bréchiforme et contiennent des veines et des débris anguleux de couleurs variées, souvent noire. L'étude de ces derniers au

microscope a permis de constater qu'ils représentent des parties intensement écrasées et refondues en verre volcanique transparent ou opaque mais conservant encore les restes de minéraux provenant de la roche: l'orthose et le quartz dans le granite, néphéline dans les syénites néphéliniques. M. Shand a donné le nom de "pseudotachylites" à ces produits de fusion. L'analyse chimique a démontré que leur composition est identique à celle de la roche cristalline ambiante.

En revenant à la météorite d'Oubari, rappelons que Stanislas Meunier en étudiant la météorite riche en matière noire de Tadjera [8], concluait qu'elle est le produit de rechauffement des minéraux contenant du fer. A. Lacroix, dans ses notes manuscrites sur les météorites, indique que les résultats de l'analyse chimique des chondrites d'Orvinio [10], de Stäldalen [5] et de Bluff [13] et des débris noires qu'elles contiennent, sont identiques. Il ajoute qu'il est évident que cette matière fondue est le résultat de l'action de la chaleur. Je citerai en outre un passage de sa note en 1926 [3]:

> "Il a été établi que la génèse des veinules est antérieure à celle de la croûte et, d'autre part, il est certain que celle-ci a été formée pendant le court trajet de la météorite dans l'atmosphère terrestre; il est donc vraisemblable que ces veinules n'ont pas pris naissance dans cette dernière. En outre, il ne parait pas indispensable de faire intervenir quelque circonstance survenue pendant la course errante de la météorite, telle que son choc avec un autre corps céleste. Peut-être serait-il plus simple de penser à une action, en quelque sorte orogénique, éffectuée dans l'astre ou les astres, d'où proviennent ces matériaux pierreux et antérieurement à leur mise en liberté dans l'espace."

La météorite de Tadjera, pour lui, est colorée en noir par le même mécanisme.

On peut rappeler à ceux qui constatent que les débris noirs sont à peu près identiques dans toutes les chondrites qu'il est naturel de voir l'olivine seule restée intacte, étant donné que les plagioclases et les pyroxènes ont leur point de fusion plus bas que celui de l'olivine.

Les grosses taches brunes, aux contours très irréguliers, que nous avons mentionnées en commençant la description de cette météorite, ont la même composition que la pierre elle-même, mais sont imprégnées par les produits d'oxydation ferrugineuse qui se propagent indifféremment au travers de tous les éléments constituants. La coloration est plus foncée vers la bordure de la tache contenant parfois au centre un grain du métal. Il est important de signaler (M.L.) que la proximité de nombreux lacs salés rend l'atmosphère de la région exceptionellement humide et explique suffisamment cette oxydation.

La *croûte noire* externe n'est pas aussi complexe que celles décrites par Brezina, Tschermak et récemment par W. Wahl [5]. On voit en plaque mince qu'elle est composée d'une bande noire, compacte, opaque et terne; elle ne renferme que rarement des grains et des poussières à éclat métallique en lumière réfléchie. On y aperçoit aussi quelques grains d'olivine; elle est bordée vers l'intérieur par une zone rubéfiée atteignant 2 mm.

Quant aux *chondres*, ils sont très nombreux dans cette météorite et de types très variés: simples, complexes, monosomatiques ou polysomatiques. Les chondres excentriques d'hypersthène ou de clinoenstatite (maclée) sont parfois très grands, ronds ou ovoïdes, avec des limites tranchées bordées par de la matière vitreuse ou par un filet d'oxydation ferrugineuse; quelquefois passant insensiblement dans la

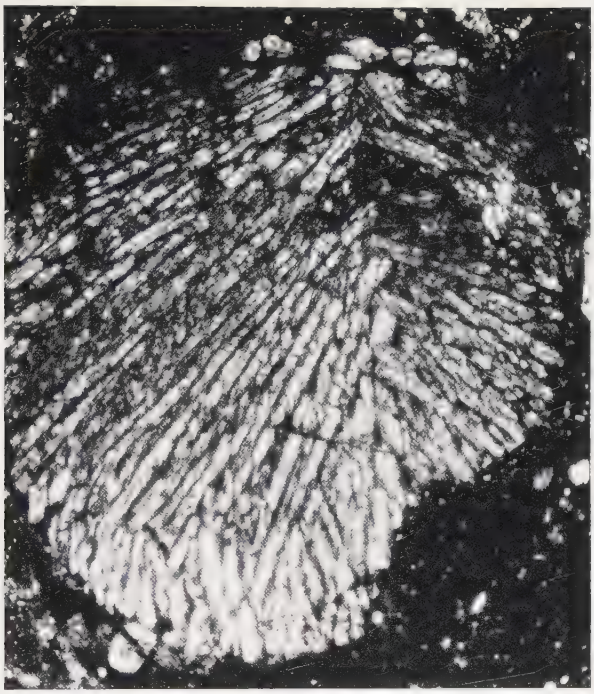

Fig. 7. Grand chondre de clinoenstatite polysomatique et excentrique. N+ Gross. 40.

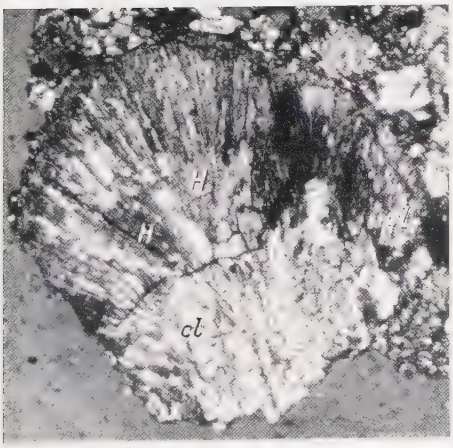


Fig. 8. Un chondre complexe composé de clinoenstatite (*cl*) et d'hypersthène (*H*). N+ Gross. 50.

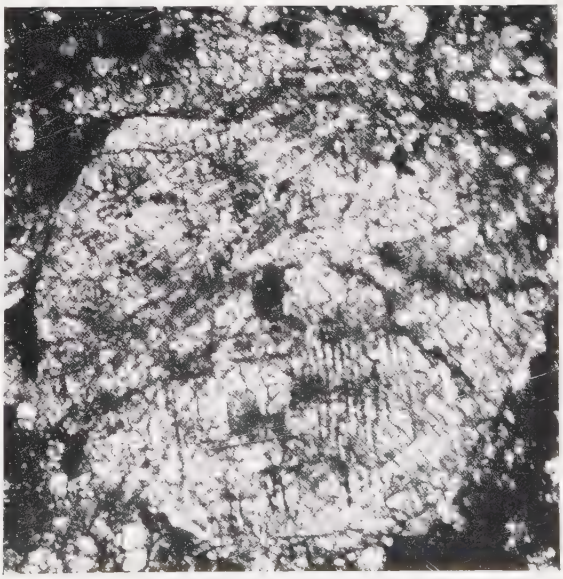

Fig. 9. Pyroxène aux contours octogonaux avec deux clivages et les fibres du méme minéral coupant ces clivages à 45°. N+ Gross. 40.

masse environnante. Il est inutile de les décrire en détail, ce serait répéter ce qui a été dit maintes fois et illustré par des photographies. Je citerai de belles planches dans G. Tschermak [9], des figures assez réussies dans W. Ramsay et L. H. Borgström [6] et enfin un travail très récent (1948) sur la structure des chondrites de A. N. Zavaritzky [14] accompagné de très nombreuses photographies dans le texte qui donnent la plupart des variétés connues. Cependant, certaines particularités trouvées dans la météorite d'Oubari méritent une mention spéciale :

Un grand chondre (2 mm), simple, mais polysomatique, est composé uniquement par des baguettes de clinoenstatite, maclées polysynthétiquement ; celles-ci partent des deux cotés d'une ligne disposée excentriquement : l'angle que font les baguettes avec cette ligne, obtus d'abord, diminue peu à peu et elles deviennent presque parallèles à l'autre bout du chondre (Fig. 7).

Un autre chondre, complexe, a comme base un large cristal de clinoenstatite (de signe optique positif, determiné avec la P.F.) s'éteignant à 40° par rapport à $n_g$ dans la section de biréfringence maximum : elle est bordée d'un coté par de l'hypersthène et de la clinoenstatite associés à axes parallèles. De ce cristal complexe partent en éventail vers la circonférence du chondre des fibres d'hypersthène et des baguettes espacées de clinoenstatite (Fig. 8) Enfin, la photographie 9 montre une section du pyroxène perpendiculaire à 2 clivages aux contours approximativement octogonaux qui se transforme en un chondre fibreux.

### 3. *Partie mètallique*

L'examen d'une surface polie en lumière réfléchie permet de reconnaître assez nettement la troïlite et le fer nickelé. M. le Professeur Orcel, qui nous a aimablement aidé dans cette étude, a confirmé en outre la présence d'un spinellide, soit la magnétite, soit la chromite ou les deux à la fois. Cependant, les grains de ce minéral sont tellement petits qu'il est impossible de les repérer pour faire une vérification. Etant donné que l'analyse chimique met en évidence une petite quantité de chrome, on peut admettre la présence de la chromite. D'autre part les taches brunes d'oxydation ferrugineuse terrestre que nous avons observées au microscope polarisant, se trouvent souvent en relation directe avec ce spinellide qui pourrait être dans ce cas de la magnétite. Le plus souvent, pourtant, le spinellide est inclus dans la zone extérieure des grains de la troïlite. La troïlite est faiblement jaunâtre et possède une biréflectance assez vive. Elle prédomine sensiblement sur le fer qui est d'un blanc-gris très brillant, complétement isotrope. Les deux forment des grains irréguliers et sont parfois associés l'un à l'autre. La troïlite remplit en outre des fissures dans les silicates, ou se présente en longs et étroits filonnets dans la pierre. Nous avons observé en un point de l'une de ces veinules un décrochement transversal suivant une petite faille. Le spinellide d'un gris peu brillant mais plus clair que celui de la gangue est isotrope entre les nicols croisés. Monsieur Orcel considère que, dans certains cas au moins, la troïlite est postérieure aux silicates et les remplace par exemple, quand elle forme un réseau anastomosé dans ceux-ci ou constitue le remplissage de veinules dans la météorite. Le fer nickelé, lui, n'a pas été trouvé sous forme de remplissage des fissures. La troïlite se rencontre aussi au centre de taches brunes d'oxydation ; très déchiquétée, elle est entourée par une matière gris-clair d'un pouvoir réflecteur faible qui est reliée à la zone de bordure composée de couches concentriques d'un gris de plus en plus sombre vers l'extérieur.

Des grains métalliques, très fins, apparaissant comme des étincelles, sont disséminés presque d'une façon homogène sur toute la surface polie; ils dessinent souvent les éléments d'un chondre et ses contours extérieurs ou suivent les plans de clivage des silicates. Cette étude montre à quel point est difficile la séparation complète de la partie métallique pour l'analyse chimique. L'analyse chimique de la chondrite d'Oubari met en évidence une concordance entre les résultats du calcul et l'observation au microscope. On y voit une faible teneur en diopside, probablement légèrement titanifère, une prédominance parmi les pyroxènes des formes magnésiennes et le minéral essentiel de la météorite—l'olivine—nettement plus riche en Mg qu'en Fe. La teneur en fer nickelé est faible pour les chondrites et se rapproche de celle des amphotérites. Nous avons choisi comme comparaison l'analyse de la météorite de Jelica. Notre collection possède de nombreuses plaques minces de cette pierre qui est certainement assez riche en chondres pour reprendre sa place parmi les chondrites (elle a été transférée dans les amphotérites

*Composition chimique*

| | *Oubari (Fezzan)** | *Jelica (Serbie)*** |
|---|---|---|
| $SiO_2$ | 38·70 | 39·72 |
| $Al_2O_3$ | 2·15 | 1·88 |
| $Fe_2O_3$ | 19·50 | 21·29 |
| MnO | 0·39 | 0·19 |
| MgO | 24·80 | 25·34 |
| CaO | 1·90 | 1·23 |
| $Na_2O$ | 0·83 | 0·12 |
| $K_2O$ | 0·19 | — |
| $TiO_2$ | 0·26 | — |
| $P_2O_5$ | 0·25 | — |
| $Cr_2O_3$ | 0·30 | 0·50 |
| $H_2O+$ | 0·22 | — |
| $H_2O-$ | 0·24 | — |
| | 89·73 | 90·27 |
| Fe | 1·80 | 1·63 |
| Ni | 0·69 | 0·83 |
| Co | 0·02 | 0·05 |
| | 2·51 | 2·51 |
| Fe | 4·48 | 4·49 |
| S | 2·56 | 2·58 |
| | 7·04 | 7·07 |

*Composition minéralogique calculée d'après l'analyse chimique*

| | *Oubari (Fezzan)** | *Jelica (Serbie)*** | | *Oubari (Fezzan)** | *Jelica (Serbie)*** |
|---|---|---|---|---|---|
| Or | 1·11 | | | | |
| Ab | 5·76 | 1·05 | Feldspaths | 9·37 | 5·76 |
| An | 2·50 | 4·73 | | | |
| $CaSiO_3$ | 2·20 | 0·58 | Pyroxène calcique et titanifère | 4·75 | 1·14 |
| $MgSiO_3$ | 1·30 | 0·30 | | | |
| $FeSiO_3$ | 0·79 | 0·26 | | | |
| $FeTiO_3$ | 0·46 | — | | | |
| $MgSiO_3$ | 10·40 | 19·80 | Pyrox. ferromagnésiens | 16·34 | 31·94 |
| $FeSiO_3$ | 5·94 | 12·14 | | | |
| $Mg_2SiO_4$ | 35·14 | 30·24 | Olivine | 57·58 | 50·84 |
| $Fe_2SiO_4$ | 22·44 | 20·60 | Chromite | 0·45 | 0·73 |
| Chromite | 0·45 | 0·73 | Merrillite | 0·74 | — |
| Merrillite | 0·74 | — | Fer métallique | 2·79 | 2·51 |
| | | | Troïlite | 7·04 | 7·7 |
| Fe, Ni, Co | 2·79 | 2·51 | | | |
| FeS | 7·04 | 7·07 | | | |

* Analysée au Laboratoire de C.N.R.S.

** Analysée par S. M. Losanitsch [4].

tout récemment). Elle a en outre la même structure bréchiforme que la chondrite d'Oubari et contient également des fragments noirs et gris clairs. Losanitsch [4] a analysé les "inclusions brunes" et trouvé qu'elles ont la même composition que la pierre elle-même.

## Conclusions

En résumé: la météorite d'Oubari (Fezzan) est une chondrite à structure cristalline, bréchiforme, pyroxéno-péridotique et sidérifère [2] pauvre en feldspath *. Profondément affectée par des actions mécaniques, elle est riche en fragments anguleux ou émoussés. Les uns, de teinte claire, sont composés de l'hypersthène englobant non seulement de l'olivine, comme c'est fréquent dans les chondrites en général, mais encore le diopside, les clinopyroxènes et parcourue par des fissures comblées par du feldspath. Les cristaux poecilitiques d'hypersthène ont été rencontrés souvent dans les chondrites, mais peut-être n'en a-t-on jamais vu d'aussi gros. D'autres portions claires montrent une mozaïque de pet ts grains cataclasés, provenant probablement des mêmes complexes et pauvres en métal. D'un grand intérêt sont des débris noirs caractérisés par une abondance de la matière vitreuse brune ou noire, qui est le résultat de l'écrasement et de la fusion des minéraux présents dans la pierre. La matière noire forme un réseau de veinules enveloppant les restes des minéraux incomplètement fondus, principalement de l'olivine. On peut comparer ces débris noirs aux "pseudotachylites" parmi le roches terrestres.

La structure bréchiforme est certainement le résultat d'un écrasement mécanique survenu en place dans le corps céleste avant son trajet dans l'atmosphère terrestre.

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* Cgb = chondrite grise bréchiforme d'après la classification de Tschermak-Brezina (1872), basée sur les caractères extérieurs des météorites. Nous préférons celle de Prior (1923), qui prend en considération principalement la composition minéralogique et la structure.

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# Association of rubidium and potassium and their abundance in common igneous rocks and meteorites*

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ABSTRACT

Spectrochemical determinations of rubidium and potassium in common igneous rock types (granite, diabase, basalt, gabbro and ultramafics) and in chondrites are given.

These determinations show that the ratio K/Rb remains virtually unchanged when proceding from rock type to rock type, and in crustal igneous rocks %K/%Rb is 90 on the average. In chondrites this ratio remains remarkably uniform (av. 100) and to within an assumed tolerance of $\pm 20\%$ is equal to that in terrestrial igneous rocks. As neither K nor Rb enters metal and sulphide phases to a significant extent, it is concluded that to within $\pm 20\%$ the ratio K/Rb in the earth as a whole is equal to that in meteoritic matter as a whole: it is believed that this is the first recorded example of such a relationship.

The abundance of potassium in chondrites is relatively uniform and appears to be considerably less than that usually given in the literature. The present determination shows that for the ultramafic rocks (mainly dunite and serpentine) the estimated abundance of potassium has to be drastically reduced. As a result, heat production by $K^{40}$ in a dunite mantle may be a small fraction, perhaps only 1/30, of that contributed by the U + Th series.

The abundance of Rb is 0·035% in crustal igneous rocks and 0·0009% in chondrites.

## Introduction

Rubidium and potassium have similar chemical properties and similar ionic radii; the radius of $Rb^+ = 1{\cdot}47$ Å, that of $K^+ = 1{\cdot}33$ Å. As a result a close association between them is to be expected, not only in terrestrial igneous rocks but conceivably also in meteorites. It is the purpose here to discuss the association of rubidium and potassium as quantitatively as possible in these materials and at the same time review and revise existing abundance values. The discussion is restricted for the most part to common igneous rock types (granite, diabase, basalt, gabbro and peridotite) and the common silicate meteorites (chondrites) which comprise 90% or so of all stones.

## Method of Analysiss

Spectrochemical methods were used for the determination of Rb and K in rocks and meteorites. Details of procedure will not be given here, but some comments will be made so as to convey an idea of the reliability and accuracy of the determinations.

Standard specimens of granite (G–1) and diabase (W–1) (see Fairbairn *et al.* [1]) have been used to prepare standards for the determination of Rb and K in all specimens. For the determination of K and Rb in rocks, working curves were prepared from G–1, W–1, and their mixtures. For meteorites, varying proportions of G–1 were mixed with one meteorite, (Homestead) and by using the addition method of plotting, K and Rb were determined in this meteorite. Once these determinations

* Part of the research described here has been supported by the Office of Naval Research, Washington, and part is from a Ph.D. thesis by W. H. Pinson

had been made, the various mixtures (G–1 and Homestead meteorite) served as standards from which working curves could be constructed for the determination of Rb and K in other meteorites. In this way all results (rocks and meteorites) are calibrated with G–1 and W–1, and systematic error, everpresent to some extent when purely synthetic stadnards are used, should be reduced to a minimum.

The assumed K concentrations in G–1 (4·6 %) and W–1 (0·59 %) are those given by Fairbairn *et al.* ([1], Table 14) based on the arithmetic mean of chemical determinations made in 24 laboratories. The recommended Rb concentrations (0·057 % in G–1 and 0·0064 % in W–1) are based on spectrochemical determinations by four analysts.

K and Rb are determined in the same spectrochemical operation. Both elements behave in much the same way in the arc discharge and should a particular determination of one of these elements be in error, a like error will be shown by the other: as a result, the ratio K/Rb will be known accurately even if the absolute concentrations are somewhat in error.

Although it is usually possible to determine the alkali metals spectrochemically with a high degree of precision, we have employed a procedure (no internal standardization) which though somewhat less precise, is easily adapted over a very wide range of concentrations, namely, 0·0002 % to 0·1 % Rb and 0·0005 % to 6 % K. The analysis lines were K $\left\{\begin{matrix}6939\\6911\end{matrix}\right.$, K $\left\{\begin{matrix}7665\\7699\end{matrix}\right.$ and Rb $\left\{\begin{matrix}7800\\7947\end{matrix}\right.$. The accuracy is adequate for this purpose and is such that when made in duplicate each result should be within +15 % −10 % of the correct value; on occasion deviations of +33 % −25 % may be encountered.

Most details of analytical procedure are described in a thesis by Pinson [2] and will be published later.

In much of the discussion in this paper we have purposely used only our own values for Rb in rocks and meteorites. This does not in any way cast doubt on the reliability of data published elsewhere and our main reason for their exclusion is to avoid introducing systematic errors by using determinations from several laboratories. A second reason is that many published determinations are listed as approximate and are therefore not suitable for our purpose. Consult Rankama and Sahama [3] for publications on the rubidium contents of rocks and minerals.

## Analytical Results and their Discussion

### *1. Granite*

Table 1 gives the rubidium and potassium contents in 29 specimens of granite from various New England states. Most are fine grained calc-alkaline granites and have been described by Dale [4], [5] and [6] and Chayes [7].

The K-Rb association is extremely close and does not appear to vary in any systematic way with possible differences in mode of origin of the granite. This is not surprising because shales (Canney, [8]) and deep ocean sediments (unpublished data from Cabot Spectrographic Laboratory) have a K/Rb ratio very similar to that in igneous rocks. Consequently possible large scale assimilation of sediments during the genesis of a granite is not likely to alter the value of the K/Rb ratio significantly from that in granite of purely igneous origin. Biotite-rich granite may show a slightly lower K/Rb ratio than average because of the facility with

which $Rb^+$ is accepted in the biotite structure. The mean ratio %K/%Rb in the suite of granite specimens is 75.

The ratio K/Cs (unpublished data) shows a much greater scatter than that of K/Rb.

*Abundance of potassium and rubidium in igneous rocks*

Much is known and much has been published on the abundance of potassium in igneous rocks, and this topic will not be discussed in detail. A few observations are of interest, however, particularly as all potassium determinations given here have been made spectrochemically.

*Table 1. Potassium and rubidium in New England granites**

| *Sample No.* | *Locality* | % K | % Rb | % K/ % Rb |
|---|---|---|---|---|
| 2 A 4 | Roadcut, Rte 128, Dedham, Mass. | 2·83 | 0·029 | 95 |
| 6 A 8 | Westwood Quarry, Westwood, Mass. | 1·77 | 0·020 | 90 |
| 15 A 2 | Bow St. Quarry, Freeport, Maine | 2·57 | 0·034 | 75 |
| 15 A 19 | Long Cove Quarry, South Thomaston, Maine | 4·34 | 0·067 | 65 |
| 15 A 23 | Meehan Quarry, Clark Island, Maine | 4·23 | 0·061 | 70 |
| 16 A 10 | American Granite Co. Quarry, North Jay, Maine | 3·30 | 0·051 | 65 |
| 16 A 12 | Maine and N. H. Granite Co. Quarry, North Jay, Me. | 3·59 | 0·063 | 55 |
| 16 A 13 | Perry Quarry, Hallowell, Maine | 3·20 | 0·050 | 65 |
| 16 A 16 | Jim Bailey Quarry, Hallowell, Maine | 4·04 | 0·058 | 70 |
| 16 A 22 | New Westerly Quarry, Milford, New Hampshire | 3·4 | 0·043 | 80 |
| 16 A 28 | Old Tonella Quarry, Milford, New Hampshire | 4·99 | 0·066 | 75 |
| 18 A 18 | Chapman Quarry, Westerly, Rhose Island | 3·17 | 0·043 | 75 |
| 18 A 25 | Calder and Carnie Quarry, Westerly, Rhode Island | 4·22 | 0·056 | 75 |
| 19 A 5 | Sullivan Granite Co. Quarry, Bradford, R. I. | 3·59 | 0·044 | 80 |
| 19 A 8 | Klondike Quarry, Bradford, Rhode Island | 4·86 | 0·073 | 65 |
| 19 A 13 | Webb-Fitzwilliam Quarry, Fitzwilliam, New Hampshire | 3·72 | 0·061 | 60 |
| 19 A 22 | North Pole Quarry, Fitzwilliam, New Hampshire. | 3·94 | 0·053 | 75 |
| 20 A 11 | Wetmore-Morse Quarry, Barre, Vermont | 3·45 | 0·045 | 75 |
| 20 A 26 | Rock of Ages Quarry, Barre, Vermont | 3·70 | 0·048 | 80 |
| 21 A 1 | Woodbury Granite Corp. Quarry, Woodbury, Vermont | 4·01 | 0·052 | 75 |
| 21 A 7 | Drennan Quarry, Woodbury, Vermont | 3·79 | 0·049 | 80 |
| 21 A 11 | Blanchard Quarry, Concord, New Hampshire | 3·84 | 0·088 | 45 |
| 21 A 16 | State Prison Quarry, Concord, New Hampshire | 3·49 | 0·076 | 45 |
| 22 A 11 | Porcupine Quarry, North Sullivan, Maine | 2·74 | 0·036 | 75 |
| 22 A 4 | Havey-Robertson Quarry, North Sullivan, Maine. | 2·39 | 0·034 | 70 |
| 24 A 20 | Blue Hill Granite Co. Quarry, Blue Hill, Maine | 3·13 | 0·053 | 60 |
| 24 A 24 | Kinch Mt. Quarry, South Brookville, Maine. | 3·10 | 0·049 | 65 |
| 25 A 12 | Booth Bros. Quarry, Jonesboro, Maine | 3·45 | 0·049 | 70 |
| G–1 | Westerly, Rhode Island | 4·50 | 0·058 | 80 |

* Kindly supplied by Dr. F. Chayes of the Geophysical Laboratory, Washington.

The average potassium content for New England granites is 3·55% (4·3% $K_2O$) and is similar to Dalys [9] average of 3·35% K (4·11% $K_2O$) for all granites. The spread is from 1·8 to 5% K. The average for basalt, gabbro and diabase analyzed

here (see below) is 0·9 %. On the basis of 2 parts granite to 1 part basalt, gabbro or diabase, as approximately representative of the composition of crustal igneous rocks, the potassium content of these igneous rocks averages 2·7 %. (In this respect, see discussion with several references by Rankama and Sahama [3] and note particularly the observations of Mead [10].) The value of 2·7 % is in agreement with that of 2·57 % given by Clarke and Washington [11] and used by Rankama and Sahama [3].

Rubidium ranges from 0·02 to 0·09 %, and averages at 0·052 % in New England granites. This magnitude may be compared with (a) average of 0·083 % for a composite sample of German granites (Goldschmidt, Bauer and Witte [12]), (b) average of 0·12 % for Rapakivi granites from Finland (Erämetsä, Sahama and Kanula [13]), (c) ranges of 0·046–0·09 % for various Basement Complex granites from southern Finland (Sahama [14]), (d) average of 0·015 % for granophyre from Skaergaard (Wager and Mitchell [15]), and (e) an average of 0·04 % for Caledonian granite and granodiorite from Western Scotland (Nockolds and Mitchell, [16]).

On the basis of 2 parts average New England granite and 1 part gabbro, diabase and basalt (see below) a rubidium abundance of 0·035 % is obtained for igneous rocks. This value is close to that of 0·031 % given by Goldschmidt, Bauer and Witte [12]. However, had they calculated their abundance as here, a considerable discrepancy would have resulted, because their average (0·083 %) for granite is 1·6 times greater than that used here.

### *2. Basalt, diabase and gabbro*

*Basalt*

Most basalt specimens are from one sill, namely, that of the Columbia River basalt as exposed east of Portland, Oregon. Specimens were collected by Drs. H. W. Fairbairn and P. M. Hurley, as described in Table 2.

*Table 2. Potassium and rubidium in basalt*

| *Sample No.* | *Locality and description* | % K | % Rb | % K/ % Rb |
|---|---|---|---|---|
| 1 | Three separate flows, Martin Lake, Goldfields, Saskatchewan | 1·7 | 0·011 | 150 |
| 2 | | 2·5 | 0·018 | 140 |
| 3 | | 1·4 | 0·008 | 175 |
| R 1429 | R 1429–R 1443. Route U.S. 30, just east of Portland, Oregon. Specimens collected at approximately regular intervals along the length of the Wahkeenah Trail, which climbs up beside Maltvomah falls and crosses section of basalt flows. Total stratigraphic section sampled ~1000 ft. Samples from massive flow centers only, and amygdaloidal and oxidized flow tops avoided | 0·58 | 0·0079 | 75 |
| R 1430 | | 0·58 | 0·0093 | 60 |
| R 1431 | | 0·66 | 0·0098 | 70 |
| R 1432 | | 0·75 | 0·011 | 70 |
| R 1433 | | 0·75 | 0·013 | 60 |
| R 1434 | | 0·75 | 0·013 | 60 |
| R 1435 | | 1·0 | 0·017 | 60 |
| R 1436 | | 1·0 | 0·018 | 55 |
| R 1437 | | 1·2 | 0·021 | 60 |
| R 1438 | | 1·0 | 0·015 | 65 |
| R 1439 | | 1·25 | 0·020 | 60 |
| R 1440 | | 1·3 | 0·016 | 85 |
| R 1441 | | 1·4 | 0·016 | 90 |
| R 1442 | | 1·25 | 0·016 | 80 |
| R 1443 | | 1·11 | 0·015 | 70 |

It may be noted that the rocks are enriched in potassium and rubidium when going from top to bottom of the sill. Potassium increases from 0·58 to 1·4% and rubidium from 0·008 to 0·021%. The ratio %K/%Rb remains almost constant and averages 70.

*Table 3. Potassium and rubidium in diabase*

| *Sample No.* | *Locality and description* | % K | % Rb | % K/ % Rb |
|---|---|---|---|---|
| 1 | Five localities within Theano Point area, Ontario | 0·82 | 0·0075 | 110 |
| 2 | | 0·75 | 0·0072 | 100 |
| 3 | | 0·75 | 0·0070 | 110 |
| 4 | | 0·65 | 0·0060 | 110 |
| 5 | | 0·50 | 0·0070 | 70 |
| 1145* | Nipissing | 0·63 | 0·010 | 65 |
| 1314 | Nipissing (granophyric) | 0·84 | 0·013 | 65 |
| 1317 | Nipissing | 1·34 | 0·018 | 75 |
| 1320 | Nipissing (granophyric) | 0·96 | 0·016 | 60 |
| 1328 | Nipissing | 0·60 | 0·013 | 45 |
| 1450a | Nipissing (granophyric) | 1·01 | 0·013 | 80 |
| 1453 | Nipissing (altered) | 0·46 | 0·007 | 65 |
| 1470 | Nipissing (granophyric) | 0·75 | 0·007 | 105 |
| 1475 | Nipissing (altered) | 1·17 | 0·018 | 65 |
| 1489 | Nipissing | 0·25 | 0·002 | 125 |
| 1493 | Nipissing (altered) | 0·56 | 0·009 | 65 |
| 1497 | Nipissing (sheared) | 0·66 | 0·015 | 45 |
| 1501 | Nipissing (olivine) | 0·93 | 0·007 | 135 |
| 1518 | Nipissing | 0·32 | 0·004 | 80 |
| 1527 | Nipissing (altered) | 0·38 | 0·004 | 95 |
| 1531 | Nipissing (granophyric) | 0·95 | 0·015 | 65 |
| 1536 | Nipissing (granophyric) | 1·34 | 0·023 | 60 |
| 1539 | Nipissing (granophyric) | 0·87 | 0·01 | 85 |
| 1542 | Nipissing | 1·23 | 0·018 | 70 |
| 1147 | Matachewan | 1·61 | 0·035 | 45 |
| 1318 | Matachewan (granophyric) | 0·97 | 0·018 | 55 |
| 1322 | Matachewan | 0·50 | 0·011 | 45 |
| 1323 | Matachewan | 0·52 | 0·008 | 65 |
| 1324 | Matachewan | 2·30 | 0·032 | 70 |
| 1352 | Matachewan | 1·67 | 0·03 | 55 |
| 1550 | Matachewan (altered) | 1·66 | 0·029 | 55 |
| 1148 | Post-Nipissing (with olivine) | 1·33 | 0·012 | 110 |
| 1506 | Post-Nipissing (with olivine) | 0·65 | 0·005 | 105 |
| 1691 | Nipigon (olivine) | 0·33 | 0·0031 | 105 |
| 1692 | Nipigon (olivine) | 0·33 | 0·0034 | 95 |
| 1693 | Nipigon | 0·46 | 0·0042 | 110 |
| 1694 | Nipigon | 0·33 | 0·0032 | 105 |
| 1695 | Nipigon (olivine) | 0·33 | 0·0032 | 105 |
| 1696 | Nipigon (olivine) | 0·21 | 0·0021 | 100 |
| 1697 | Nipigon | 0·21 | 0·0025 | 85 |
| 1698 | Nipigon (olivine) | 0·33 | 0·0034 | 95 |
| 1699 | Nipigon (olivine) | 0·46 | 0·0042 | 90 |

* Greater locality detail for Nipissing, post-Nipissing, Matachewan and Nipigon samples from Ontario will be given in a forthcoming publication on the abundance and distribution of several rarer elements in these rocks.

Basalt from Goldfields, Saskatchewan is potash-rich; the ratio %K/%Rb averages at 150.

*Diabase*

Various varieties of diabase, including granophyric and olivine-rich types, are represented, as shown in Table 3. Specimens from Nipigon are characterized by a low concentration of potassium (0·21–0·46 %) and of rubidium (0·0021–0·005 %); the ratio %K/%Rb remains almost exactly constant for this suite of specimens and averages 100. For all diabase specimens, the ratio %K/%Rb varies from 45 to 125 and averages 80.

*Gabbro*

Gabbro is represented by four specimens from the well-known Skaergaard layered intrusion (Wager and Deer [17], kindly furnished by Prof. L. R. Wager, and one from Duluth. Included with these four Skaergaard specimens were other rock types, the whole forming a fairly representative suite of specimens. All determinations are given in Table 4.

*Table 4. Potassium and rubidium in Skaergaard rocks*

| *Sample No.* | *Description* | % K | % Rb | % K/ % Rb |
|---|---|---|---|---|
| 3058 | Acid granophyre | 3·06 | 0·024 | 130 |
| 359 | Melanocratic acid granophyre | 2·60 | 0·022 | 120 |
| 1905 | Basic hedenbergite granophyre | 1·01 | 0·007 | 140 |
| 4142 | Fayalite ferro-gabbro | 0·72 | 0·006 | 120 |
| 1907 | Hortonolite ferro-gabbro | 0·27 | 0·0015 | 180 |
| 3661 | Gabbro without olivine | 0·30 | 0·0016 | 190 |
| 4067 | Olivine gabbro | 0·24 | 0·0017 | 140 |
| 1208 | Gabbro from Duluth | 0·79 | 0·01 | 80 |

The ratio K/Rb remains virtually unchanged when passing from one rock type to another in the Skaergaard suite, and is not detectably influenced by differentiation. The mean ratio %K/%Rb = 140; in the specimen from Duluth, the ratio is 80. For chemical determinations of potassium and other spectrochemical determinations of rubidium in these and allied specimens from Skaergaard, see Wager and Mitchell [15].

The distribution of several elements in some Swiss rocks, mainly spilitic lavas from Kärpf (Glarus) has been investigated by G. C. Amstutz (data as yet unpublished). The ratio %K/%Rb was found to remain almost constant and averages at about 85.

### *3. Ultramafic rocks*

Results of the analyses of 12 ultramafic rocks are given in Table 5. The seven specimens numbered P–140 to P–391 were kindly supplied by Dr. G. L. Davis (Geophysical Laboratory, Washington). Radioactivity measurements and a petrographic description of these specimens are given by Davis and Hess [18].

Potassium and rubidium are characteristically low in all specimens except those that are biotite-rich.

*Table 5. Potassium and rubidium in ultramafic rocks*

| *Sample No.* | *Description* | % K | % Rb | % K/ % Rb |
|---|---|---|---|---|
| P 140 | Dunite, Balsam, Gap, N. C. | ~0·001 | <0·0002 | — |
| P 141 | Serpentine, Geiger's Quarry, Wash. | ~0·0005 | < 0·0002 | — |
| P 145 | Dunite, Twin Sisters Mt., Whatson Wash. | ~0·0004 | <0·0002 | — |
| P 318 | Serpentine, Belvedere Mt., Vermont | ~0·003 | <0·0002 | — |
| P 320 | Serpentenized dunite, King's Mine, Thetford, P. Q. | ~0·003 | <0·0002 | — |
| P 369 | Websterite, Webster, N. C. | ~0·011 | <0·0002 | — |
| P 391 | Dunite, Addie, N. C. | ~0·004 | <0·0002 | — |
| Sc–10 | Lherzolite, Baltimore, Md. | ~0·015 | <0·0002 | |
| S–57 | Pyroxenite, Webster, N. C. | ~0·001 | <0·0002 | — |
| — | Saxonite, Riddle, Oregon | ~0·004 | <0·0002 | — |
| S–44 | Anorthosite, Split Rock, Minn. | 0·05 | 0·0005 | 100 |
| S–49 | Mica augite peridotite, Murfreesboro, Ark. | 4·6 | 0·11 | 42 |
| — | Kimberlite, S. Africa | 1·7 | 0·038 | 61 |

Most of the above mica-free peridotites belong to Hess [19] third group—the so-called Alpine peridotites, occurring as isolated masses frequently associated with orogenic zones and considered by Hess as representative of a primary peridotitic magma. In these specimens, the potassium abundance averages ~0·004 % K. This figure merely indicates an order of magnitude because such low concentrations of potassium had not been anticipated on the basis of previous chemical determinations of potassium in peridotite, and consequently an accurate spectrochemical procedure was not at hand. This general magnitude should, however, be reliable, and is almost ten times lower than the value of 0·03 % K given by Daly for average dunite. It is not known to what extent the mode of origin of dunite might influence its potassium content. The geophysical consequences of lowering the abundance of potassium in dunite, and the difficulties of its chemical determination at extremely low concentrations, are topics which are discussed below.

The concentration of rubidium is below its detection limit (<0·0002 %) in most specimens. In mica-augite from Arkansas and Kimberlite from South Africa, the ratio K/Rb is somewhat lower than is usual in common rock types and is attributed to the fact that the biotite structure accepts $Rb^+$ more readily than other potassium minerals. See for example determinations by Nockolds and Mitchell [16] and determinations and discussion by Whiting [20].

### *4. Stony meteorites*

Potassium and rubidium were determined in 26 meteorites, comprising 21 chondrites, olivine from a pallasite, one chladnite, and three tektites. These specimens from the *Harvard Museum*, were kindly furnished by Dr. Clifford Frondel. Because of their common occurrence, chondrites may be regarded as representative of silicate meteoritic material as a whole, and particular attention was given them. All determinations are given in Table 6.

Potassium and rubidium are presumably held structurally in plagioclase, usually present to some extent in chondrites, and in maskelynite, the glassy interstitial material between and included in the chondrules.

*Table 6*

| *Locality and description* | % K | % Rb | % K/ % Rb |
|---|---|---|---|
| (a) *Potassium and rubidium in chondrites* | | | |
| Homestead*, Iowa (brecciated grey bronzite) | 0·11 | 0·0012 | 85 |
| Rancome, Rancome's Bridge, North Carolina (spherical) | 0·13 | 0·0014 | 95 |
| Hayes Center, Nebraska (spherical) | 0·07 | 0·0006 | 115 |
| Waconda, Kansas (brecciated spherical hypersthene) | 0·09 | 0·0010 | 90 |
| Assun, France (spherical) | 0·10 | 0·0011 | 90 |
| Holbrook, Arizona (crystalline spherical hypersthene) | 0·08 | 0·0008 | 100 |
| Bjurbole, Finland (spherical hypersthene) | 0·10 | 0·0009 | 90 |
| Pultusk, Poland (veined grey bronzite) | 0·06 | 0·0005 | 120 |
| Forest City, Iowa (brecciated spherical bronzite) | 0·05 | 0·0006 | 85 |
| Hessle, Sweden (spherical bronzite) | 0·08 | 0·0006 | 130 |
| Kernouve, France (veined crystalline bronzite) | 0·09 | 0·0007 | 130 |
| Barratta, New South Wales (black) | 0·12 | 0·0013 | 90 |
| Mocs, Transylvania (veined white hypersthene) | 0·11 | 0·0010 | 110 |
| Tennasilon, Estonia (veined spherical hypersthene) | 0·10 | 0·0008 | 125 |
| Monroe, North Carolina (veined grey bronzite) | 0·07 | 0·0007 | 100 |
| Long Island, Kansas (veined intermediate hypersthene) | 0·06 | 0·0010 | 60 |
| Beaver Creek, British Columbia (crystalline spherical) | 0·08 | 0·0006 | 130 |
| Lumpkin, Georgia (crystalline spherical hypersthene) | 0·06 | 0·0007 | 85 |
| Cangas de Onis, Spain (spherical hypersthene) | 0·08 | 0·0008 | 100 |
| Estacado, Texas (crystalline bronzite) | 0·07 | 0·0006 | 115 |
| Warrentown, Missouri (spherical hypersthene) | 0·06 | 0·0006 | 100 |
| (b) *Potassium and rubidium in tektites and other meteorites* | | | |
| Olivine from pallasite | <0·001 | <0·0002 | — |
| Chladnite, Johnstown | 0·001 | <0·0002 | — |
| Tektite, Annam, Indo China | 1·74 | 0·019 | 90 |
| Tektite, N. Cambodia, Indo China | 1·74 | 0·018 | 95 |
| Tektite, P. I. | 1·83 | 0·018 | 100 |

* Complete bibliographies of these meteorites are on file in the mineralogical section of the *Harvard University Museum*.

*Potassium*

The lowest concentration of potassium is present in olivine from pallasite (<0·001 %) and in chladnite (bronzite), with 0·001 %. Such extremely low concentrations may be compared with similar concentrations in mica-free ultramafic rocks described above. The three tektites show an average concentration of 2·3 % K, which is very similar to the value of 2·1 % given by Linck [21].

In chondrites, potassium concentration ranges from 0·05 % to 0·13 %, and averages at 0·09 % K. This concentration variation is small, and expressed as a percentage spread (see Brown and Patterson [22]) is 24 %. It must be borne in mind that the reproducibility of the spectrochemical procedure allows a maximum tolerance of 4/3 to 3/4 for each determination, and hence the concentration scatter is probably smaller than is indicated in Table 6. Wahl [23] has emphasized the early observation of Nordenskiöld [24] that chondrites are commonly of uniform composition and states that extreme values for alkali metals are open to serious question. We have found that uniformity of concentration is characteristic not only of K, but

also of such minor constituents as Rb (see below) and Sc, Sr, Ba and Zr (unpublished data; see PINSON [2]).

From a statistical analysis of 107 published analyses of silicate meteorites, BROWN and PATTERSON [22] found that the degree of uniformity of concentration of different elements in the silicate phase varied with their absolute abundance: those that were most abundant (Si, for example) showed much less scatter than those that were relatively rare (Co, for example). Our investigations on K, Sc, Sr, Ba, and Zr do not support this and show that not only do chondrites appear to be of uniform composition, but that concentration variation from specimen to specimen is independent of the abundance of the element. The abundance range covered by the elements noted above is from 0·1 % for potassium (see below) to 0·0007 % for scandium. There are three possible causes for the disagreement between the conclusions made here and those of BROWN and PATTERSON [22]:

*Table 7. Comparison of flame photometer and spectrochemical determinations of potassium*

| *Meteorite* | *Spec.* (% K) | *Flame phot.* (% K) |
|---|---|---|
| Homestead . . . . | 0·11 | 0·12 |
| Hayes' Center . . . | 0·07 | 0·096 |
| Kernouve . . . . . | 0·09 | 0·11 |

(a) their statistical examination included all silicate meteorites, whereas our statistical observations are restricted to chondrites.

(b) the elements we investigated are characteristically those which are restricted to the silicate phase, whereas some of those discussed by BROWN and PATTERSON,

(c) ever-present analytical error, which is likely to increase with decrease in concentration, if, as has been common, chemical methods of analysis are used. cobalt for example, are constituents of the sulphide and metal phases also, and.

The abundance and distribution of Sc, Sr, Ba and Zr in chondrites will be discussed in detail later.

The average abundance value of 0·09 % K for chondrites is to be compared with a value of 0·20 % for silicate phase (corrected for sulphide and metal phases) given by BROWN and PATTERSON [22]; see also MERRILL [25], and GOLDSCHMIDT [26] and adopted by RANKAMA and SAHAMA [3]. If correction is made for the presence of sulphide and metal (*cf.* BROWN and PATTERSON [22]), our value of 0·09 % is increased to about 0·1 %. The difference between the two values (0·1 and 0·2 %) is large and the cause as yet unknown. All previous determinations were made by wet chemical methods.

In order to check the spectrochemical determinations, Miss G. SULLIVAN of the Geology Department, M.I.T., kindly determined potassium flame photometrically in three specimens of chondrite; her results, together with the spectrochemical determinations, are compared in Table 7.

Agreement is good and supports the potassium abundance found spectrochemically. However, this point cannot be regarded as settled, because despite flame photometer support, it must be borne in mind that potassium has been determined chemically in many chondrites by several competent chemical analysts and the fact that the majority, though certainly not all, of these determinations give a considerably higher potassium concentration cannot be disregarded.

Direct comparison between chemical and spectrochemical determinations are sometimes possible and these are given in Table 8.

It is difficult to draw a definite conclusion from the comparison in Table 8 other than that the wide range of variation of chemical determinations indicates some serious analytical errors. The chemical determinations have been made by several analysts, and in this respect it is instructive to examine modern potassium determinations in chondrites as made by a single analyst. Table 9 gives six such determinations by H. B. Wiik.

*Table 8. A comparison of some chemical determinations of* K, *as given by* Brown *and* Patterson [22] *with spectrochemical determinations given here*

| *Description* | *Chem.* (% K) | *Spec.* (% K) |
|---|---|---|
| Homestead, Iowa . . | 0·13 | 0·11 |
| Holbrook*, Ariz. . . | tr. | 0·08 |
| Bjurbole, Finland . . | 0·30 | 0·10 |
| Forest City, Iowa . . | 0·065 | 0·05 |
| Hessle, Sweden . . . | — | 0·08 |
| Kernouve, France . . | tr. | 0·09 |
| Mocs, Rumania . . . | 0·19 | 0·11 |
| Tennasilm, Esthonia . | ($Na_2O + K_2O$ 2·61 %) | 0·10 |
| Monroe, N. C. . . . . | — | 0·07 |
| Long Island, Kan. . | 0·024 | 0·06 |
| Beaver Creek, Can. . | 0·11 | 0·08 |
| Estacado, Tex. . . . | 0·32 | 0·07 |
| Johnstown**, Col. . . | 0·08 | 0·001 |

* See also analysis by H. B. Wiik in Table 9 below.

** Chladnite (bronzite).

Although only a limited number of specimens have been analyzed, they show a far greater uniformity of concentration than shown by the chemical determinations in Table 8, and in this respect they accord with the spectrochemical determinations given in this paper. The average of 0·17 % in Table 9 is still, however, considerably greater than the spectrochemical value. Specimens 3–5 average at 0·14 %. The spectrochemical determination of K in No. 5 is 0·08 %.

*Table 9. Chemical determinations of potassium in six chondrites*

| *No.* | *Locality* | % K |
|---|---|---|
| 1 | Misshof | 0·23 |
| 2 | McKinney | 0·18 |
| 3 | Collescipoli | 0·20 |
| 4 | Knyahinya | 0·14 |
| 5 | Holbrook | 0·13 |
| 6 | Selma | 0·14 |
| | | Av. 0·17 |

Nos. 1–5, Wahl [23] and No. 6, Wahl and Wiik [27].

Although we have purposely attempted to avoid systematic error in the spectrochemical determinations, some such error may be present, but it is doubtful whether systematic error could be more than +30 %. This would set the maximum upper limit to our abundance value as 0·13 %.

Apart from the fact that some of the chemical determinations, mainly the older ones, are probably obviously in error, consideration must be given to the possibility that some systematic and random error is present in recent determinations. The so-called Lawrence Smith procedure is susually employed for alkali metal determinations and the importance of blank error and its accurate correction becomes increasingly urgent at low concentrations. This is a point much emphasized by Groves [28], p. 78) who gives the example of a blank determination he made on $CaCO_3$ and $NH_4Cl$ of "A.R" grade from a well-known firm. 0·11 % $K_2O$ was found, mainly in the $CaCO_3$. Such a blank is usually subtracted, but if omitted would double the amount of potassium determined in a chondrite. However, even if the subtraction is made, the determinations could hardly be regarded as of superior quality because blank and unknown concentrations may be of the same magnitude.

Many analysts attempt to free their reagent $CaCO_3$ from impurity potassium by repeated washing with hot water. Further error in a chemical determination of potassium in chondrite might be caused by a large ratio of Na to K (X 5–10) and this would tend to give a high value.

Because of the importance of the potassium abundance in chondrites for a discussion on the origin of the earth and of its subsequent history, it is highly desirable that further investigations be carried out in which a selected suite of chondrites is analyzed by several competent analysts using different methods.

In dunites and serpentine where the potassium concentration is frequently much less than in chondrites (often $< 0{\cdot}01\,\%$, see above), chemical determinations have little significance, even if attempts have been made to make accurate blank corrections and to remove potassium from $CaCO_3$. As a result a value of 0·03 % K for average dunite based on chemical determinations, probably has little or no meaning at all. In this respect the difference between the chemical value of 0·08 % K for chladnite from Johnstown (see Table 8) as compared with 0·001 % found spectrochemically is significant.

*Rubidium*

Noddack and Noddack [29] give an abundance of 0·00045 % Rb for the silicate phase of meteorites. This value is based on a composite sample: the method of analysis is not given. The abundance value given here, (arithmetic mean of Rb determinations in chondrites given in Table 6) is 0·0009 % for chondrites and 0·001 % after correction for metal plus sulphide. The variation of concentration from specimen to specimen is small and the same as for potassium. Variation of K and Rb is usually sympathetic and consequently the ratio K/Rb remains virtually constant within the limits of experimental error. The mean ratio K/Rb is 100 and is close to that for the common rock types described above. This topic is discussed in detail below.

*5. Small volume residuals*

As used here, this term embraces pegmatitic minerals (all stages of fractionation and replacement), aplite dykes, small feldspar veinlets and sometimes granophyre. Although such materials are not classed under common rock types, some comments on the K-Rb association in them will be made here insofar as it is pertinent. It is well known that the ratio K/Rb is frequently much less in these materials than in common rock types and reaches a minimum in potassium minerals characteristic of late stage replacement in complex pegmatites. For example, in lepidolite, the ratio %K/%Rb averages 6 and may on occasion be as low as 3. It is not known whether such enrichment of rubidium relative to potassium is restricted to pegmatites only or whether it represents continuation of a trend already begun in a differentiated suite of parental rocks. From the discussion above on the K/Rb association in common rock types, it appears that the ratio K/Rb is constant, or at least very nearly so, during the major phases of differentiation. The Skaergaard rocks are particularly pertinent in this respect. A very small degree of enrichment of Rb relative to K might not, of course, be detected in the analysis of the rocks themselves. Because, however, of the small quantity of pegmatite or other residual material, such a slight enrichment of Rb relative to K during differentiation of a large parental mass could yield a relatively high concentration of Rb. In any event, enrichment

of Rb relative to K in small volume residuals is not significant for this discussion because of the small volume of such bodies when compared with that of the common igneous rock types.

### 6. *The ratio* K/Rb *in common igneous rocks and in meteorites*

The close association of K and Rb is displayed graphically in Fig. 1. A straight line appears to show the closest fit. The slope of this line is not exactly unity, but it is doubtful whether this small departure from unity should be interpreted as indicating a slight overall enrichment of Rb to K when progressing from chondrites to basic rocks (diabase, basalt and gabbro) and finally to granite; a slight adjustment of the spectrochemical working curves could, for example, give a unit slope in Fig. 1. A slight enrichment of Rb relative to K may be expected because the radius of $Rb^+$ (1·47 Å) is larger than that of $K^+$ (1·33 Å) and because it seems to be well established that in pegmatites, Rb is markedly enriched in K minerals of late formation. One possible cause why Rb shows little if any enrichment in rocks is that prevailing temperatures and pressures are much higher than in residual stages of replacement fractionation in a pegmatite.

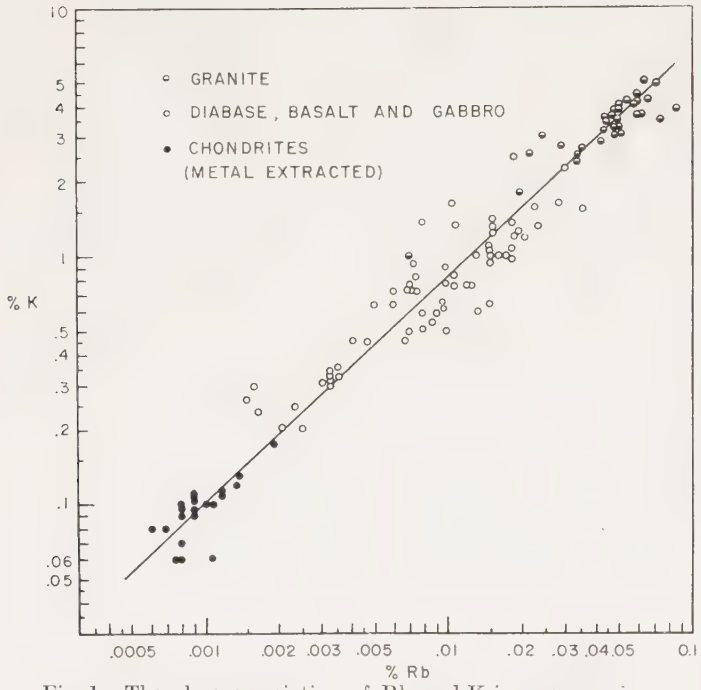


Fig. 1. The close association of Rb and K in common igneous rocks and in chondrites is readily seen in this figure. It is doubtful whether the slope of slightly less than 45° is significant; see discussion in text.

*Table 10. Average* % K/% Rb *ratios (various rocks and localities)*

| | |
|---|---|
| New England granites | 75 |
| Basalt | 75 |
| Goldfields | 70 |
| Columbia River | 150 |
| Diabase | |
| Nipigon | 100 |
| Matachewan | 55 |
| Theano Point | 100 |
| Others, mainly Nipissing | 80 |
| Skaergaard rocks, mainly gabbro | 140 |
| Av. | 90 |

The mean ratio of K/Rb in rocks has been computed as follows. Table 10 shows the average ratio for any given rock type for each principal area that has been investigated. The average of these is taken as representing the value % K/% Rb for igneous rocks as a whole.

The weighting is arbitrary and thus the average of 75 for New England granites is given twice merely because a large area is covered. Actually it matters little whether such arbitrary weighting as given in Table 10 is used or whether each

individual determination given in this paper is averaged; respective average ratios %K/%Rb calculate as 90 (Table 10) and 85.

The value of 90 is very close to that of 100 for chondrites. If we allow a tolerance of 20% for analytical and sampling error, we may state that to within these limits the ratio K/Rb is the same in common igneous rock types and chondrites. Furthermore, as neither potassium nor rubidium is accepted to any significant extent in either metal or sulphide phases, this statement may be extended to include the earth as a whole and meteorites as a whole.

*The primitive ratio* K/Rb

Both K and Rb are radioactive. $K^{40}$ ($\beta^-$ and electron capture) and $Rb^{87}$ ($\beta^-$) are the unstable isotopes, the respective half lives of which may be taken as $1{\cdot}3 \times 10^9$ years (Sawyer and Wiedenbeck [30]; see discussion and bibliography by Birch [31] and $5{\cdot}9 \times 10^{10}$ years (see discussion and bibliography by Ahrens [32]). The half-life difference is considerable and as that of $K^{40}$ is fairly short when compared with an assumed magnitude of $3 \times 10^9$ years for the age of the earth, these radioactivities should be given consideration in a discussion of the K/Rb ratio. $K^{40}$ is, however, rare. It is now 0·011% of total potassium, and it is only at an age of about ten half lives ($1{\cdot}3 \times 10^{10}$ years) that the proportion of $K^{40}$ in total potassium becomes large (11%) and would therefore influence a primitive K/Rb ratio; that is, the ratio at time of formation of earth or meteorite. As the age of the earth and the age (or ages) of meteorites is probably much less than such a magnitude, one may conclude that the ratio $\frac{\text{total K}}{\text{total Rb}}$ as determined now in rocks and meteorites is virtually the same as when earth and meteorites were formed. The ratio of the active isotopes, $K^{40}/Rb^{87}$, has of course changed significantly.

### 7. *Heat generated by* $K^{40}$ *in a dunite mantle*

Calculations by Birch [31] show that if we assume an average abundance of 2·6% K for a crust of about 33 km depth (approximate total mass $= 47 \times 10^{24}$ g of which $1{\cdot}5 \times 10^{20}$ g is $K^{40}$) and an average abundance of 0·03% K for dunite (Daly [9]) in a mantle extending to some 2900 km (approximate total mass $= 4000 \times 10^{24}$ gm of which $1{\cdot}6 \times 10^{20}$ g is $K^{40}$), then the amount of heat generated by $K^{40}$ is about the same in each, namely, $0{\cdot}32 \times 10^{20}$ cal/year for crust and $0{\cdot}35 \times 10^{20}$ cal/year for mantle. If we assume that the ultramafics investigated here are roughly representative of the mantle and that although the average K content of these rocks (0·004%) is approximate it represents a correct magnitude, it follows that the total heat generated by $K^{40}$ in a dunite mantle is small compared with that generated in the crust.

$K^{40}$ heat production in the crust is about 1/6 of that of the U + Th series (Birch [31]). In a dunite mantle with 0·03% K, however, it may be shown (Birch [31]) that the heat contribution by $K^{40}$ is approximately 1/3 of that of the U + Th series. This calculation is based on the Ra content of dunite as given by Davis [33] and on the assumption that the U and Th series generate equal amounts of heat. A reduction of K in the mantle from 0·03% to $\sim$0·004% would reduce the heat contribution of $K^{40}$ to a small fraction of that produced by the U + Th series.

*Production of* $A^{40}$ *from* $K^{40}$ *in the mantle*

On the basis of a 0·03% abundance of K in the mantle it follows from the above figures (Birch [31]) that $A^{40}$ production in mantle and crust are about the same. Assuming an age magnitude of $3300 \times 10^6$ years for the earth, Birch calculates the $A^{40}$ mass for crust and mantle, respectively, as $0{\cdot}9 \times 10^{20}$ g and $1{\cdot}0 \times 10^{20}$ g. If a magnitude of 0·004% is substituted for 0·03%, production of $A^{40}$ in the mantle becomes small compared with that in the crust.

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# Variations in the relative abundance of the carbon isotopes in plants*

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ABSTRACT

The $C^{12}/C^{13}$ ratio of 105 plants representing all the major systematic groups has been determined. Except perhaps for gymnosperms there are in principle no systematic differences between the groups. Characteristic differences occur, however, between plants grown in different biotopes, and these differences are related to the varying intensity of the local carbon-dioxide cycle.

## Introduction

A. O. Nier and his co-workers [1], [2] have shown that the isotopic composition of carbon in living matter and related materials is different from that in carbonates. So far the number of investigated plants is small, and in a compilation made by K. Rankama [3] in 1948 only seven examples of present day plants are presented. This material is too limited to be used as a starting-point for geochemical calculations of the circulation of carbon in nature, and in an effort to fill this gap in our knowledge the present investigation was started.

## The Material

The material consisted of plants from the herbarium of the Riksmuseum in Stockholm which had been preserved for periods of time varying between 1 and 115 years. However, this circumstance seems to have no influence on the results, judging from the fact that these do not vary systematically with the "herbarium age" of the plant. This is not surprising if it is remembered that the preparation of a plant for a herbarium is merely a drying process.

The plants were burned with oxygen in a combustion furnace by A. Parvel using the same technique as described by S. Landergren and A. Parvel [11]. Those plants containing calcium carbonate, *e.g. Chara*, were treated with acid before being burned in order to avoid contamination from occluded calcium carbonate.

The mass spectrometric measurements were performed by R. Ryhage at the Department of Chemistry of the Karolinska Institut. The reproducibility of the measurements is within $\pm 0{\cdot}1$ unit, in most cases within about $\pm 0{\cdot}05$ unit. The results are referred to the same standard sample used in the earlier papers of this series [4], [5], [6].

Originally the intention was to have common representatives of all the major plant groups. Furthermore, the same species was to be represented by plants grown in very different surroundings, *e.g.* plants from the Northern and Southern limits of their distribution.

The results obtained were so interesting, however, that the material had to be completed using ecological instead of systematic viewpoints. They are presented in Table 1.

* Paper No. 5 in a series devoted to the application of isotope ratios to geological problems.

*Table 1*

*Abbreviations:* m = marine; d = desert plant; l = lacustrine; tr = tropical rain forest plant

| *No.* | *Name and locality* | | $C^{12}/C^{13}$ |
|---|---|---|---|
| | ***Chlorophyceae*** | | |
| 1 | *Ulva lactuca*, Malmö, Sweden | m | 89·19 |
| 2 | *Ulva lactuca*, f. *adnata*, Venice, Italy | m | 89·74 |
| | ***Charophyceae*** | | |
| 3 | *Chara crinita*, Ivetofta, Skåne, Sweden | m | 89·37 |
| 4 | *Chara foetida*, Salta, Argentine | l | 90·30 |
| 5 | *Chara fragilis*, Lake Ringsjön, Sweden | l | 90·03 |
| 6 | *Chara jubata*, "Parsteiner See," Angermünde, Germany | l | 90·03 |
| 7 | *Chara tomentosa*, Öregrund, Sweden | m | 90·03 |
| | ***Phaeophyceae*** | | |
| 8 | *Fucus furcatus*, f. *variabilis*, Sitka, Alaska | m | 89·90 |
| 9 | *Fucus vesiculosus*, Varberg, Sweden | m | 89·57 |
| 10 | *Macrocystis pyrifera*, between St. Paul and Amsterdam, Atlantic Ocean | m | 90·18 |
| 11 | *Sargassum globulariaefolium*, Sidney, New South Wales | m | 89·97 |
| 12 | *Sargassum natans*, Sargasso Sea, Atlantic Ocean | m | 89·70 |
| | ***Rhodophyceae*** | | |
| 13 | *Chondrus crispus*, Kristineberg, Bohuslän, Sweden | m | 90·15 |
| 14 | *Chondrus crispus*, Digby Neck, Nova Scotia | m | 89·52 |
| | ***Fungi*** | | |
| 15 | *Cantharellus cibarius*, Bringetofta, Sweden | | 90·85 |
| 16 | *Cantharellus cibarius*, Mariefred, Sweden | | 90·66 |
| | ***Bryophyta*** | | |
| | *1. Hepaticae* | | |
| 17 | *Marchantia berteroana*, Puyehue, Osorno, Chile | | 90·91 |
| 18 | *Marchantia polymorpha*, Halltorp, Småland, Sweden | | 90·89 |
| 19 | *Marchantia*, Tasmania | | 90·85 |
| 20 | *Plagiochila asplenioides*, Hjulserud, Sweden | | 90·89 |
| 21 | *Plagiochila cava*, Caldas, Minas Geraës, Brazil | | 90·78 |
| | *2. Musci* | | |
| 22 | *Hylocomium splendens*, Ryd, Västergötland, Sweden | | 90·76 |
| 23 | *Mnium seligeri*, Rydboholm, Uppland, Sweden | | 90·88 |
| 24 | *Sphagnum falcatulum*, Fiordo Martinez, Bahia Plüschow, Chile | | 90·55 |
| 25 | *Sphagnum girgensohnii*, Ydre, Sweden | | 90·96 |
| 26 | *Sphagnum*, Tasmania | | 91·37 |
| | ***Pteridophyta*** | | |
| | *1. Lycopodinae* | | |
| 27 | *Lycopodium selago*, Caldas, Minas Geraës, Brazil | | 90·79 |
| 28 | *Lycopodium selago*, Rostock, Dalsland, Sweden | | 91·03 |
| 29 | *Selaginella selaginoides*, Forssa, Hälsingland, Sweden | | 90·72 |
| 30 | *Selaginella selaginoides*, Canada | | 90·84 |
| | *2. Filices* | | |
| 31 | *Cyathea australis*, Atherton Tableland, N. Queensland | | 90·96 |
| 32 | *Dryopteris thelypteris*, Danderyd, Sweden | | 90·99 |
| 33 | *Dryopteris thelypteris*, SE side of Kilimanjaro, East Africa | | 90·58 |

*Table 1. (Continued)*

| No. | Name and locality | | $C^{12}/C^{13}$ |
|---|---|---|---|
| | ***Phanerogamae*** | | |
| | **A. Gymnospermae** | | |
| | *1. Cycadinae* | | |
| 34 | *Cycas media*, Darwin, N. Terr., Australia | | 90·48 |
| | *2. Ginkgoinae* | | |
| 35 | *Ginkgo biloba*, Kiangsi, China | | 90·70 |
| | *3. Coniferae* | | |
| 36 | *Araucaria angustifolia*, Rio Grande do Sul, Brazil | | 90·62 |
| 37 | *Araucaria biramulata*, New Caledonia | | 90·49 |
| 38 | *Picea abies*, Täby, Uppland, Sweden | | 90·67 |
| 39 | *Picea esperata*, Radja and Yellow River gorges, Eastern Tibet | | 90·80 |
| 40 | *Pinus silvestris*, NW of Troizkosavsk, Transbaikalia | | 90·54 |
| 41 | *Podocarpus gracilion*, Kirstenbosch, Cape Province, S. Africa | | 90·62 |
| 42 | *Podocarpus totara*, Waitakera Hills, North Island, New Zealand | | 90·53 |
| | **B. Angiospermae** | | |
| | a) Dictyledoneae | | |
| | *1. Polycarpicae* | | |
| 43 | *Brasenia schreberi*, Fish Lake, Chisago Co., Minn., U.S.A. | l | 89·25 |
| 44 | *Trigynaea ecuadorensis*, between Tena and Napo, Prov. Napo Pastaza, Ecuador | tr | 91·27 |
| 45 | *Virola paponis*, Tingo Maria, Prov. Huánuco, Peru | tr | 90·88 |
| | *2. Polygonales* | | |
| 46 | *Calligonum acanthopterum*, var. *setosa*, between Annaju and Gnaurs, Askhabad | d | 89·63 |
| | *3. Centrospermae* | | |
| 47 | *Arthrophytum arborescens*, Repetek, Merv, Transcaspia | d | 89·66 |
| 48 | *Haloxylon aphyllum*, Central Asia | d | 89·66 |
| 49 | *Salsola richteri*, Repetek, Transcaspia | d | 89·69 |
| 50 | *Stellaria media*, Ljusterö, Sweden | | 90·87 |
| 51 | *Stellaria media*, Misserghin, Algeria | | 90·81 |
| | *4. Parietales* | | |
| 52 | *Leonia cymosa*, Iquitos, Dep. Loreto, Peru | tr | 91·09 |
| 53 | *Tamarix androssowii*, Amu-Darya, Turkestan | d | 90·71 |
| | *5. Guttiferales* | | |
| 54 | *Chrysochlamys weberbaueri*, Tingo Maria, Dep. Huánuco, Peru | tr | 91·12 |
| 55 | *Dipterocarpus alatus*, near Calcutta, Bengalia, India | | 90·72 |
| | *6. Rosales* | | |
| 56 | *Astragalus paucijugus*, Uch-Ajji, Transcaspia | d | 90·66 |
| 57 | *Entadopsis polyphylla*, Iquitos, Dep. Loreto, Peru | tr | 91·12 |
| 58 | *Sclerolobium*, Tingo Maria, Dep. Huánuco, Peru | tr | 90·71 |
| | *7. Podostemonales* | | |
| 59 | *Podostemum ceratophyllum*, on rocks, St. Regis River, Hogansburg, Franklin Co., N. Y. | l | 90·30 |

*Table 1. (Continued)*

| No. | Name and locality | | $C^{12}/C^{13}$ |
|---|---|---|---|
| | *8. Myrtales* | | |
| 60 | *Eucalyptus melliodora*, Warrumbungle Ranges, New South Wales | | 90·78 |
| 61 | *Eucalyptus polyanthemos*, Canberra, Australia | | 91·10 |
| 62 | *Eugenia buxifolia*, Key West, Florida, U.S.A. | | 90·70 |
| 63 | *Eugenia microphylla*, Lantao Island, Kwangtung, China | | 90·87 |
| 64 | *Metrosideros angustifolia*, Bosch Kloof, South Africa | | 90·71 |
| 65 | *Metrosideros polymorpha*, subsp. *incana*, Huehue, Island of Hawaii. | | 90·88 |
| 66 | *Myriophyllum verticilatum*, Åtvidaberg, Sweden | l | 91·16 |
| 67 | *Hippuris vulgaris*, Friggesund at River Svåga, Hälsingland, Sweden | l | 91·01 |
| | *9. Fagales* | | |
| 68 | *Betula*, Karlstad, Sweden | | 90·89 |
| 69 | *Betula ermani*, Petropavlovsk, Kamtchatka, twig | | 91·04 |
| 70 | *Betula ermani*, Petropavlovsk, Kamtchatka, leaf | | 90·90 |
| 71 | *Nothofagus betuloides*, Punta Arenas, Patagonia | | 90·56 |
| 72 | *Quercus ilex*, Djebel Ballota, Tunis | | 90·70 |
| 73 | *Quercus robur*, Risinge, Östergötland, Sweden | | 90·87 |
| | *10. Urticales* | | |
| 74 | *Ficus paraensis*, Quistococha, Iquitos, Dep. Loreto, Peru | tr | 91·09 |
| 75 | *Olmedia aspera*, Tingo Maria, Dep. Huánuco, Peru | tr | 91·07 |
| | *11. Proteales* | | |
| 76 | *Protea abyssinica*, Monte Bizen, Eritrea | | 90·80 |
| 77 | *Protea marginata*, Karoo Poort, South Africa | | 90·62 |
| | *12. Terebintales* | | |
| 78 | *Picrolemma sprucei*, Iquitos, Dep. Loreto, Peru | tr | 91·06 |
| | *13. Tubiflorae* | | |
| 79 | *Cordia nodosa*, Tingo Maria, Dep. Huánuco, Peru | tr | 91·43 |
| 80 | *Jacaranda copaia*, Tingo Maria, Dep. Huánuco, Peru | tr | 91·01 |
| | *14. Rubiales* | | |
| 81 | *Sommera sabiceoides*, Hacienda Soledad, Iquitos, Dep. Loreto, Peru | tr | 91·27 |
| | *15. Campanulatae* | | |
| 82 | *Lobelia dortmanna*, Lake Lillsjön, Vrena, Södermanland, Sweden | l | 90·74 |
| | b) Monocotyledoneae | | |
| | *1. Helobiae* | | |
| 83 | *Butomus umbellatus*, Lake Kolbotten, Nacka, Sweden | l | 90·86 |
| 84 | *Elodea canadensis*, Flottsund, Uppsala, Sweden | l | 90·27 |
| 85 | *Vallisneria americana*, Farleip Point, Cayuga Lake, N. Y. | l | 89·91 |
| | *2. Potamogetonales* | | |
| 86 | *Najas marina*, Laduviken, Stockholm, Sweden | l | 90·18 |
| 87 | *Potamogeton densus*, Irrigation canal, Damascus, Syria | l | 90·85 |
| 88 | *Potamogeton natans*, Ensta damm, Gamla Uppsala, Sweden | l | 90·51 |
| 89 | *Potamogeton pectinatus*, the Sea S of Skillinge, Skåne, Sweden | m | 89·47 |
| 90 | *Potamogeton polygonus*, Caldas, Minas Geraës, Brazil | l | 91·05 |
| 91 | *Zostera marina*, Buccarizza, Fiume | m | 89·84 |
| 92 | *Zostera marina*, v. *angustifolia*, Styrsö, Bohuslän, Sweden | m | 89·32 |

*Table 1. (Continued)*

| *No.* | *Name and locality* | | $C^{12}/C^{13}$ |
|---|---|---|---|
| | *3. Principes* | | |
| 93 | *Desmoncus prunifer*, Iquitos, Dep. Loreto, Peru . . . . . | tr | 90·89 |
| | *4. Synanthae* | | |
| 94 | *Carludovica palmata*, Hacienda Clementina on Rio Pita, Prov. Los Rios, Peru . . . . . | tr | 91·39 |
| | *5. Spathiflorae* | | |
| 95 | *Lemna minor*, Mälsåker, Södermanland, Sweden . . . . . | 1 | 91·04 |
| 96 | *Wolffia arrhiza*, Stagnant water at Dunaharaszti, Danube, Roumania | 1 | 90·88 |
| | *6. Panales* | | |
| 97 | *Typha angustifolia*, Lake Norrsjön, Bladåker, Uppland, Sweden . . | 1 | 90·86 |
| | *7. Glumiflorae* | | |
| 98 | *Lasciacis ligulata*, San Juan, Iquitos, Dep. Loreto, Peru . . . . . | tr | 91·07 |
| 99 | *Paspalum distichum*, Stanford Univ. Lake, Santa Clara Co., Cal, U.S.A. | 1 | 89·51 |
| 100 | *Paspalum distichum*, Fischhoek, Cape Peninsula, South Africa . . . | 1 | 89·53 |
| | *8. Cyperales* | | |
| 101 | *Carex incurva*, Andes NW of San Juan, North Argentine . . . . | | 90·59 |
| 102 | *Carex leporina*, Kärna, Bohuslän, Sweden . . . . . | | 90·79 |
| 103 | *Diplasia karatifolia*, Tingo Maria, Dep. Huánuco, Peru . . . . . | tr | 91·24 |
| | *9. Bromeliales* | | |
| 104 | *Guzmania eduardi*, Hacienda Clementina on Rio Pita, Prov. Los Rios, Peru . . . . . | tr | 90·64 |
| | *10. Liliiflorae* | | |
| 105 | *Eichhornia crassipes*, in the swamp "La Siganea," Catelina, Pinar del Rio, Cuba . . . . . | 1 | 90·91 |

## Preliminary Discussion of the Results

The results of Nier and his co-workers indicated that there might be large variations in the $C^{12}/C^{13}$ ratio of plants, and Table 1 is a confirmation of their results.

There are several examples of the same species from two different localities, but they do not show any definite relationship between isotope ratio and latitude, as can be seen from Table 2. It might therefore be concluded that the ambient temperature is of no primary importance.

On the other hand if the material is divided into several groups such as marine plants, limnic plants, terrestrial plants from tropical rain-forests, desert plants, and other terrestrial plants, the distribution shown in Fig. 1 will be obtained.

From this figure it is quite evident that some of the groups are quite homogeneous, especially marine plants, tropical rain-forest trees, and the group "other terrestrial plants." If this last-mentioned group is divided into three main subgroups: angiosperms, gymnosperms and cryptogames, it is interesting to note that two of the three groups show almost identical distributions, but that the third one, *i.e.* gymnosperms, systematically gives somewhat lower ratios. Whether this trend is real or is due only to an unfavourable selection of plants, is impossible to determine with

*Table 2*

| *Plant species* | *Locality* | *Approx. latitude* | $C^{12}/C^{13}$ |
|---|---|---|---|
| *Ulva lactuca* | Italy | 45° N | 89·74 |
| | Sweden | 55° N | 89·19 |
| *Chondrus crispus* | Nova Scotia | 45° N | 89·52 |
| | Sweden | 60° N | 90·15 |
| *Cantharellus cibarius* | Bringetofta, Sweden | 58° N | 90·85 |
| | Mariefred, Sweden | 59 °N | 90·66 |
| *Lycopodium selago* | Brazil | 20° S | 90·79 |
| | Sweden | 60° N | 91·03 |
| *Selaginella selaginoides* | Canada | 50° ? N | 90·84 |
| | Sweden | 60° N | 90·72 |
| *Dryopteris thelypteris* | East Africa | 5° S | 90·58 |
| | Sweden | 60° N | 90·99 |
| *Stellaria media* | Algeria | 35° N | 90·81 |
| | Sweden | 60° N | 90·87 |
| *Paspalum distichum* | California | 35° N | 89·51 |
| | South Africa | 35° S | 89·53 |

any degree of certainty from the limited material so far studied, but it may quite well be that this trend really exists.

The desert plants show two well-defined groups of values. It is interesting to note that the 89·6-group grew in real deserts, the 90·6-group in one case close to a river, in the other at a railway station.

The limnic plants form a very heterogeneous group. It consists of (a) plants which are rooted at the bottom and raised into the air at the top, and (b) submerged hydrophytes which live in deeper water. The emergent hydrophytes usually contain less chlorophyll in the submerged portion than in the portion above water.

We may regard the floating hydrophytes, which are rooted to the bottom but float their foliage upon the surface of the water, as a transition stage between these two groups. In all three cases the water in which the plants live may be stagnant or not.

In Table 3 the limnic plants have been classified according to the above-mentioned properties, and an inspection of this table shows that isotope ratios around 91 are found for all plants living in stagnant water. On the other hand most submerged plants living in non-stagnant water give values under 90·5, and the emergent hydrophytes also form an inhomogeneous group (Fig. 2).

Before discussing these results it might be profitable to recapitulate a few facts about the local carbon dioxide cycle.

## The Cycle of Carbon with Special Reference to Plants

For over a hundred years the cycle of carbon in nature has been studied by practically all kinds of scientists, and it is now known that it consists of a series of smaller cycles forming a rather intricate system.

*Table 3*

| *No. (Table 1)* | *Name* | *1* | *2* | $C^{12}/C^{13}$ |
|---|---|---|---|---|
| 43 | *Brasenia schreberi* | f | ns | 89·25 |
| 83 | *Butomus umbellatus* | e | ns | 90·86 |
| 4 | *Chara foetida* | s | ns | 90·30 |
| 5 | *Chara fragilis* | s | ns | 90·03 |
| 6 | *Chara jubata* | s | ns | 90·03 |
| 105 | *Eichhornia crassipes* | f | s | 90·91 |
| 84 | *Eloeda canadensis* | s | ns | 90·27 |
| 67 | *Hippuris vulgaris* | e/s | s/ns | 91·01 |
| 95 | *Lemna minor* | f | (s) | 91·04 |
| 82 | *Lobelia dortmanna* | s | ns | 90·74 |
| 66 | *Myriophyllum verticilatum* | s | s | 91·16 |
| 86 | *Najas marina* | s | ns | 90·18 |
| 99, 100 | *Paspalum distichum* | e | ns | 89·51, 89·53 |
| 59 | *Podostemum ceratophyllum* | (s) | ns | 90·30 |
| 87 | *Potamogeton densus* | s | s | 90·85 |
| 88 | *Potamogeton natans* | f | ns | 90·51 |
| 90 | *Potamogeton polygonus* | s | s | 91·05 |
| 97 | *Typha angustifolia* | e | s/ns | 90·86 |
| 85 | *Vallisneria americana* | s | ns | 89·91 |
| 96 | *Wolffia arrhiza* | f | s | 90·88 |

1. e = emergent hydrophyte; f = floating hydrophyte; s = submersed hydrophyte.
2. s = living in stagnant water; ns = living in non-stagnant water.

In the present paper we are concerned only with plants and therefore all other aspects of the carbon cycle will be neglected.

The terrestrial plants obtain their carbon dioxide from the air, the mean content of which is about 0·03 vol %. Depending on local factors which hardly can be accounted for in all specific cases, large variations around this mean value have been observed.

However, some regularities have been noticed which are of special interest in connection with the carbon-dioxide fixation by plants. Von Fodor in 1881 was the first to observe that there is a daily periodicity in the $CO_2$ content of air, the maximum occuring during the night and the minimum during day time. This pronounced effect shows that the mixing between the main atmospheric air and the air layers close to the ground is not instantaneous, *i.e.* that diffusion is a slow process.

It is also well-known that the air layer in immediate contact with the soil is enriched in carbon dioxide. The reason for this is that the soil produces carbon dioxide partly by the respiration of the microorganisms in the soil itself and partly by the respiration of the plant roots. There seems to be general agreement among botanists that the assimilation and production of carbon dioxide in a forest or other biotope are normally in equilibrium with each other.

The soil, the atmosphere and the plants constitute the participants of the local cycle of carbon which is characteristic of plant life. Of course, their relative importance varies according to local conditions. Of great interest in this cycle is its completeness, *i.e.* to what degree the soil carbon-dioxide is directly assimilated by the plants. It is obvious from what has been said above that this process is

more complete if the plants are low-grown and live in an area under lee, especially if the carbon-dioxide production of the soil is high. On the other hand if a plant lives isolated from other plants in a windy place on an oceanic island, or in sand without much soil, it will generally obtain practically all of its carbon-dioxide supply from the main atmospheric air.

These two examples are extreme cases, and as a rule conditions are somewhere in-between. Probably the first case will be most closely realized in a tropical rain-forest, and the second in a desert.

For hydrophytes there are several cases which should be discussed separately. First of all there are the emergent hydrophytes which are rooted to the bottom of the lake or the sea, but assimilate mainly atmospheric carbon dioxide. In most respects they are equivalent to terrestrial plants, except for one thing which will be discussed below. The second group consists of submersed plants and the third of floating hydrophytes. This third group, to which *e.g.* water-lilies belong, are probably closely related to the second one, because they do not extend to any height above the water surface, and it might confidently be assumed that the carbon dioxide content of a very thin layer close to the water surface will be determined by the carbon dioxide of the water.

The submersed plants obtain their supply of carbon dioxide from the water. As is well-known, water contains carbonate ions, bicarbonate ions and dissolved carbon dioxide gas. There has been much discussion among botanists and physiologists as to whether the plants assimilate the gas exclusively, or whether they are able to use the ions directly. For the present discussion this point is not important, since we are primarily interested in isotope ratios which will not vary on account of the exchange of carbon atoms between the different molecules and ions.

The total content of carbon dioxide in sea water varies greatly, but a normal value is about 0·5 vol %, *i.e.* the concentration is about ten times as high as in the atmosphere. In lakes and rivers the content is also greatly variable, but for pure water in contact with air the content is about 0·03 vol %, which means that it is the same as in air. If the partial pressure of carbon dioxide is higher the amount of gas in the water will be larger, and the same is true if the water is buffered by the presence of carbonates.

In the open sea the carbon dioxide, produced at the bottom by microorganisms and by the respiration of plants and animals, will not have the same possibility to influence directly the assimilation of submersed and emergent plants partly on account of the circulation of water by currents and partly on the high content of carbon dioxide present in sea water. However in a small stagnant part of the sea or lake or in a small pond, the conditions for a submersed plant will be almost the same as for a terrestrial plant. There will be an exchange of carbon dioxide with the atmosphere, and perhaps also by convection currents with the main part of the water basin. Finally there will be a supply of carbon dioxide with the ground-water, and this source might be of special importance in the case of small spring-water lakes without influx.

If limestone is present in the area where the plant is living some of the assimilated carbon dioxide might derive from disintegrated or dissolved rock material. The importance of this factor will of course vary considerably according to local circumstances.

## Discussion of the Results with Special Reference to the Cycle of Carbon Dioxide

According to a statement of Weigl [9] (cited after [8]) the assimilation rate of $C^{14}O_2$ is about 17 % less than that of $C^{12}O_2$. Probably this would correspond to a value somewhat around 5 % in the case of $C^{13}O_2$, which is a very serious discrepancy if one remembers that the *maximum* enrichment found in the present investigation is about 2 %. Weigls experiments are, however, very difficult to perform, on account of the simultaneous respiration and reassimilation of carbon dioxide by the plant, and his results cannot therefore be regarded as conclusive. The results of the present and earlier measurements on plants confirm, however, the reality of such a difference in the assimilation rates of the carbon dioxide molecules, but the observed effects are small.

It might be asked whether the difference in the assimilation rates is alone responsible for the complete enrichment (one-step process), or whether the cycle of carbon dioxide, too, is essential in order to obtain the observed enrichments (cyclic process).

Assuming the first alternative to be correct there are two possible theories. First, it might be thought that the difference in assimilation rates varies from species to species, or perhaps from plant to plant. Large differences should then be expected between *e.g.* ordinary plants, and xerophytes, and especially hydrophytes. In spite of the fact that there is a difference between desert plants and terrestrial plants in general, it is not likely that there is a large difference between an ordinary leaf and a succulent one for the following reason. The essential process of assimilation is going on in the mesoderm on an atomic scale, while the constructional differences between the ordinary and the succulent leaf are, in comparison, on a macro scale. Furthermore there are no typical differences in the anatomy of submersed plants living in stagnant and non-stagnant water. This is contrary to expectations, if it is remembered that one of the most obvious results of the present investigation is that such differences are typical. Therefore I have rejected this hypothesis, and it is assumed that the assimilation rates do not vary very much for different plants species; always allowing for a systematic difference between ordinary terrestrial plants and submersed ones, and perhaps for gymnosperms in comparison to other plants.

The second possibility is that this systematic difference in assimilation rates is large and that the observed isotope effects depend on the completeness of the assimilation. A one-step rate process proceeds best with incomplete reactions: *i.e.* the isotope effect will be maximum if the favoured molecules are drawn from material that is continously being replaced with fresh material. If the reaction is complete there will be no enrichment at all. Consequently it must be concluded that according to this theory the most favourable places for enrichment are deserts and other windy places and the most unfavourable surroundings tropical rainforests, etc. Using the same argument it can be shown that the enrichment observed for submersed plants in stagnant water should be less than that for plants living in non-stagnant water. A glance at Figs. 1 and 2 shows the incorrectness of these conclusions.

Consequently we are forced to investigate whether the cyclic exchange of carbon dioxide already discussed in the previous paragraph might explain the observed

values. For terrestrial plants the situation can be described in the following way (Fig. 3). Carbon dioxide is assimilated by the plant from the local air with slightly different reaction rates for $C^{12}O_2$ and $C^{13}O_2$, then stored in the plant for some time and eventually returning to the air from the soil, partly through the respiration of the plant and partly through the metabolism of the microorganisms. All the time

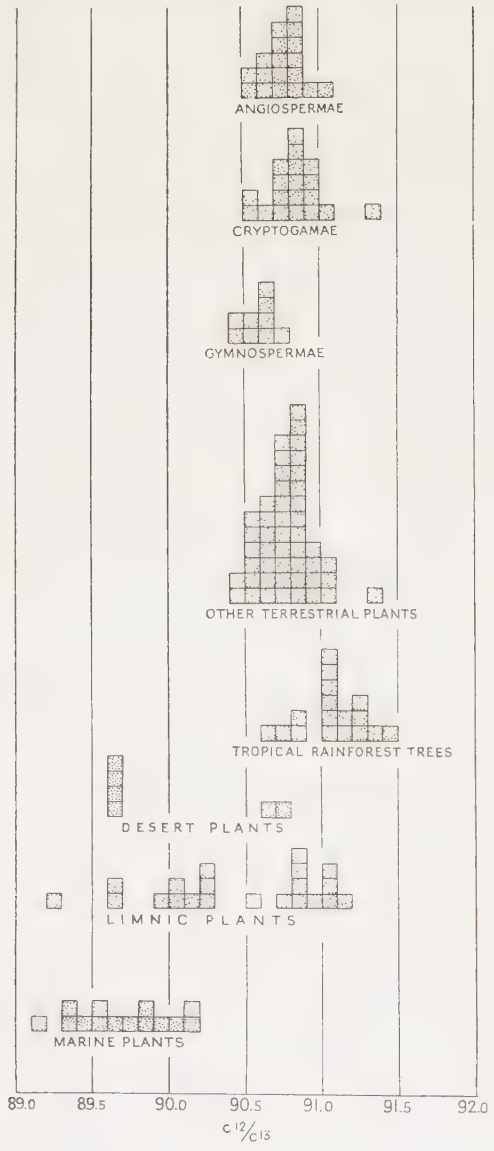


Fig. 1.

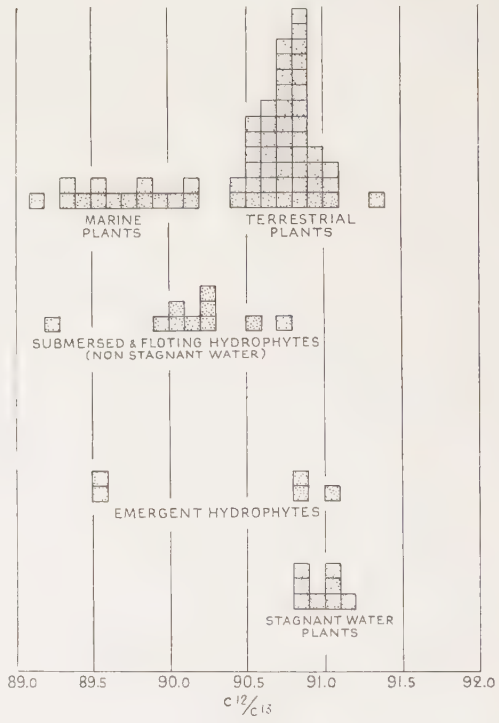


Fig. 2.

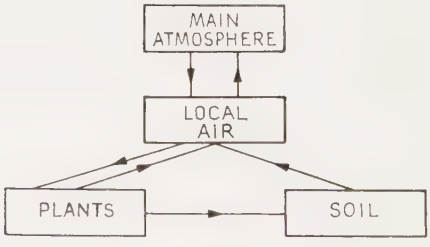


Fig. 3.

there is an exchange of carbon dioxide between the local and the main atmosphere. These conditions are equivalent to those used in cyclic isotope enrichment processes.

According to this theory the enrichment will be smallest where the "soil respiration" is negligible and where the "local atmosphere" for some reason or other does not develop, *i.e.* in a desert or at a constantly windy place. The largest isotope

effect will be observed where the cyclic process is most intense, *e.g.* a tropical rain-forest. This is in accordance with the observations as can be seen from Fig. 1. The four lowest values observed in the main series of terrestrial plants (90·5–90·6) are from plants which have grown at notoriously windy places (24, 33, 71 and 101). In the sea and in lakes and rivers the cyclic process will develop in stagnant water (Fig. 4), but not normally in non-stagnant. This is also in accordance with the observations.

If there is a supply of carbon dioxide originating from limestone, the enrichment normally will be smaller, because the ratios observed for limestones are mostly around 89 or somewhat lower. The influence of this source varies in accordance with local conditions. This point has not been investigated, but there is no reason to doubt the reliability of this conclusion. Probably some of the author's plant values are influenced by this factor, but it is impossible to prove anything without a thorough knowledge of the exact place where the plants have grown. It might also be expected that the enrichment will vary with the height from the ground in a biotope, being largest close to the ground and smallest at the tops of high trees. The reason for this is, of course, that the exchange with the main atmosphere by winds will be largest at the tops of high trees. Also, the enrichment will not be constant in space and time because the conditions will vary from place to place and from season to season.

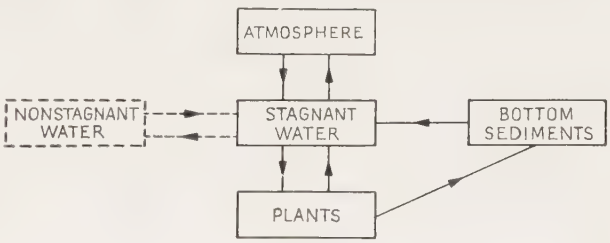

Fig. 4.

An essential point in this type of enrichment is that the cycle should not be quite complete, but that there should always be an exchange with the bulk of the atmosphere or sea-water. Without this exchange the enrichment will stop.

The observed variations in the ratio are not very large, but the variations will be accentuated for the heavy isotope C–14. It is very likely that in the future these cyclic enrichment factors have to be taken into account. Especially dangerous is, of course, contamination with "fossil carbon dioxide" which is free from radio-activity [10].

The possibilities of investigating the history of early life on earth are of course somewhat modified by the results of the present investigation. On the other hand, it seems most natural to assume that life was first created in stagnant water, and if this hypothesis is correct there is a fairly good chance of tracing life far back into pre-Cambrian times.

## Summary and General Conclusions

In the preceding paragraphs it has been shown that enrichment of the light carbon isotope in plants, which was discovered by Nier, is intimately connected with the cycle of carbon dioxide. This explains why in places where the cycle cannot develop, *e.g.* in the open sea or in deserts, enrichment is much less than in places where the cycle is more complete and intense, *e.g.* in tropical rain-forests or stagnant water.

The variations in the isotope ratio of carbon is thus not primarily a problem of systematic botany but of ecology. In order to study the influence of the various factors in natural surroundings, ecologists and physiologists probably have to cooperate. This is especially important in testing the observed anomaly of gymnosperms.

The question immediately arises of what is happening to the plant isotope ratio when it is transferred to the animal kingdom. Will the ratio change in the animal body or not? At present I am investigating some typical aspects of this problem.

It is also interesting to speculate about the possibilities of observing variations in the ratios of other stable elements. It is obvious that the chances for enrichment increase if there is a cyclic process in operation. But in order to obtain a large isotope effect it is very important that the amount of material of an element taking part in a cycle is not large and that the cycle is repeated rapidly. This is not the case in most cyclic processes in the earth's crust. Furthermore there must be an exchange of material with a major source of the element. This means that it is probably nitrogen which, besides carbon, oxygen and hydrogen is the most favourable case, assuming of course that there is a difference in the reaction rates of the nitrogen bacteria.

In the main, however, the favourable circumstances met with in the case of carbon must be rare.

*Acknowledgement*—The present investigation has been supported by a grant from *Statens Naturvetenskapliga Forskningsråd*. Not being a botanist myself I have been privileged to receive help and advice in the selection of suitable species from my colleagues at the Botanical Departments of the *Riksmuseum*, Prof. E. Hultén, Prof. O. H. Selling, Dr. E. Asplund, Dr. S. Ahlner and Dr. H. Horn af Rantzien.

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# Book reviews

**Geochemistry** by K. Rankama and T. G. Sahama. University of Chicago Press and Cambridge University Press, pp. i–xvi and 912. 1950. £5 12s. 6d.

This work on Geochemistry has grown out of a much smaller book written by Professor Sahama in Finnish and published during the war. The authors in their preface state that it is not intended as a textbook for students nor as a comprehensive account of all geochemical information, but in the opinion of the reviewer, it will, if used with discretion, serve both these ends for some time to come. It is the first comprehensive book on geochemistry to appear in English since the publication of Clarke's Data of Geochemistry, which, appearing in 1908, was brought up to date in successive editions until 1924. There is no doubt that Professors Rankama and Sahama have produced a work which lays under a great debt of gratitude all those interested in geochemistry and the many related fields of science.

Between the wars V. M. Goldschmidt and his many collaborators were responsible for greatly increasing the amount of available geochemical data and, at the same time, Goldschmidt's powerful mind was able to make bold and imaginative advances in our understanding of the principles governing the distribution of chemical elements in the Earth. The whole way of thinking in geochemistry in the last 25 years has been largely conditioned by Goldschmidt's work and the present volume is no exception. Before his death in 1947 Goldschmidt had almost completed a book on geochemistry which has since been eagerly awaited. Although the volume under review includes more recent data it is still most important that Goldschmidt's own book should be published, since it will give us the final views of a master worker in geochemistry and a picture of the subject as he left it in 1945.

In a preliminary section Rankama and Sahama give an historical outline of the science of geochemistry which, in a work of this size, might well have been fuller. They also discuss the question "What is Geochemistry?" and provide definitions of geochemistry from Clarke, Vernadsky, Fersman and Goldschmidt. Perhaps the brief definition by Vernadsky is the most effective:—"La géochemie étudie les éléments chimiques dans l'écorce terrestre et autant qu'il est possible dans le globe terrestre. Elle étudie leur histoire, leur distribution dans le temps et l'espace." The authors, however, mainly propose to follow Goldschmidt's definition of the science which he formulated by indicating the three following tasks of geochemistry:

1. To establish the abundance relationships of elements and nuclides in the Earth.

2. To account for the distribution of elements in the geochemical spheres of the Earth, *e.g.*, in the minerals and rocks of the lithosphere and in natural products of various kinds.

3. To detect the laws governing the abundance relationships and the distribution of the elements.

This way of defining geochemistry fails to give sufficient emphasis to the historical aspect and in this sense seems to fall short of Vernadsky's.

Geochemistry is a study on a wide plane and it is not easy to define neatly its scope and its relationships to other sciences. In the opinion of the reviewer however, one thing is certain and that is that geochemistry, despite its name, is not a variety of chemistry. Chemistry is a fundamental science which could be investigated in any convenient corner of the Universe equally as well as on the Earth. Geochemistry is a particular study of this planet and is thus less fundamental than chemistry itself. Geochemistry is a kind of applied science, all the branches of chemistry and physics which are helpful being applied to the specific problem of the chemistry of the Earth. Although limited in one way therefore, in another it is of very wide scope because, like the rest of geology, it is an historical science and is concerned with the changes in the distribution of the elements in the Earth throughout the long period of time since the planet became a distinct entity. It is a part geology since chemistry is not concerned with the time factor in this way.

Although Rankama and Sahama give no very clear answer to their question "What is Geochemistry?" this has not prevented the rest of the book covering satisfactorily the field of geochemistry as it is understood today. The plan of the book is to present in the first half, under the heading General Geochemistry, a discussion of the distribution of the elements in the major units of the Earth. For the composition of the deep interior the usual analogy with meteorites is followed. Then comes consideration of the so-called lithosphere, that is, the accessible igneous and sedimentary rocks, and this is followed by consideration of the hydrosphere, atmosphere and biosphere. The first part of the book concludes with a chapter on Cosmochemistry in relation to Geochemistry and a chapter giving an outline of the Geochemical Evolution of the Earth. Part II of the book is a consideration of the manner of occurrence of the elements treated either individually or in related groups. As each part consists of about 400 pages, the reviewer would put in a plea for the next edition being published as two separate volumes.

In considering the abundance of the elements in the Earth, average values for igneous rocks and meteorites are used as a basis, as has been done by CLARKE, WASHINGTON, GOLDSCHMIDT and others. The so-called average composition of the lithosphere, obtained by averaging all igneous rocks, gives, no doubt, a first approach to the composition of the continental areas down to a depth of say 10 miles, but without more geological knowledge of the ocean areas it is unsatisfactory to give this as the average for the whole lithosphere. When the composition of the depths of the Earth are considered every thing depends on the particular hypothesis adopted and particularly on the attitude taken to KUHN and RITTMANN'S suggestion that the core consists of undifferentiated planetary material. The authors state that this hypothesis should attract more attention, as indeed it has in the recent work of RAMSEY and others (*cf.* Nature, Vol. 165, p. 218). The authors deal with the views on the nature of the deeper part of the Earth with fairness and leave the subject, as they necessarily must, all very much in the air.

The chapter on the Geochemistry of the Lithosphere consists of 170 pages. It seems that the authors felt that they must treat the lithosphere as a unit because they believe a cyclic process to be important which involves both the igneous and sedimentary parts of the lithosphere. In the opinion of the reviewer the sedimentary rocks may be as legitimately treated separately as the ocean or atmosphere.

The first part of the chapter on the Geochemistry of the Lithosphere deals with the geochemical characterization of the elements, a subject considered at some length in the previous chapter, where GOLDSCHMIDT'S classification into siderophile, chalcophile and lithophile is given and discussed. The introduction by the authors of the words oxyphile and sulphophile for elements which tend to enter oxygen compounds on the one hand and sulphides and other oxygen-free compounds on the other, seems to be of doubtful value. It does not make it any more possible to divide the elements rigorously into two groups. The tendency of elements to enter various typical lattice environments varies gradually and what is needed is a method of numerical evaluation of the tendency based on some experimentally determinable date. The application of crystal chemistry to the composition and stability relations of the crystals separating from magma is considered in the next section, GOLDSCHMIDT'S now well-known principles forming the basis for the discussion. The words *diadochy* and *diadochic* are introduced following STRUNZ, but seem to express nothing more than the word replacement. We may say that Fe and Mg ions are diadochic in silicates but why not, more simply, that Fe and Mg ions replace each other in silicates ? It is courageous of the authors to consider and to attempt to explain the composition of the more important rock-forming minerals merely in a section of this chapter. Some attempt at this had to be made in order to deal with the section on the geological significance of fractional crystallization which follows. This section on fractional crystallization can hardly be expected to please petrologists who know the insecure basis for the generalizations which necessarily have to be made if the matter is to be dealt with briefly, but there is a real danger that the treatment given may lead chemist to take much too simple a view of the problem of the origin of the intermediate and acid rocks. The late stages in the supposed fractional crystallization series are more securely based and the geochemical treatment of the pegmatites is convincing.

External earth processes, mainly weathering and subsequent redistribution of materials as sediments or as soluble substances in the sea is described by the authors as the *minor cycle*. This process is not cyclic; it is what GOLDSCHMIDT called the third or exogenic stage of geochemical differentiation, and it is essentially a change in one direction from igneous rocks to sedimentary. GOLDSCHMITDs geochemical classification of the sedimentary rocks is adopted and a good discussion is given of the factors causing changes in concentration of the elements during the external Earth processes, such as the structure of the clay minerals and the role of hydrogen ion concentration, of oxidation-reduction potentials, of sorption and base exchange. The section on the total quantities of sediments on the Earth gives GOLDSCHMIDT'S figures obtained essentially by the methods first used by J. JOLY and later by F. W. CLARKE, a point which deserves mention. KUENEN'S recent important contribution, taking into consideration the probable amounts of the deep-sea sediments, is briefly noted.

In a final section of this long chapter on the lithosphere the authors consider the geochemical aspects of metamorphism and metasomatism. Metamorphism in the usual sense does not involve significant changes in the bulk chemical composition, while metasomatism, of course, does. There seems no need to substitute for these well-defined words the more unwieldy "internal metamorphism" and "metasomatic metamorphism". The terminology of the geological sciences is surely complex enough and no important new idea is implied by the suggested new names. It is useful to have the authors' consideration of the geochemical implications of metasomatic processes although they rightly say that the available

information is "still very scarce and incomplete". This is a tricky subject at the present time, but the brief review of the possible ways in which diffusion of substances may take place in rocks and the importance in this connection of the vapour pressure and surface tension of the various possible crystal phases and of the effect of the size and other properties of the migrating ions and atoms is usefully discussed. It is obviously necessary to deal with the difficult subject of the relation between granites and metasomatic processes. It seems, however, unbalanced to describe as the *major cycle of the lithopshere*, the weathering of igneous rocks, the formation of sediments and their conversion back again to rock melt. Some granites no doubt result from metasomatism of sedimentary rocks, and others perhaps by metasomatism followed by remelting, but surely there is not, and never has been sufficient sedimentary material in the Earth to make is likely that this is responsible for so large a part of the granites of the lithosphere as to make it reasonable to describe this as the major cycle of the lithosphere, while the processes giving the sedimentary rocks is called the minor cycle. The authors give their idea in the form of a diagram showing rock melt solidifying to igneous rock, which, by weathering and transport, gives sedimentary rocks, these in turn being converted into migmatites and eventually remelted, thus completing the cycle. From this diagram the authors omit what, in the opinion of the reviewer, is the most important process of all, namely, the direct remelting of igneous rock, perhaps with some metasomatism, to give rock melt or magma. In making their geochemical calculations on the amounts of sediment on the Earth both CLARKE and GOLDSCHMIDT have ignored any effect due to the conversion of sedimentary rock into granite and this treatment is probably still justified, considering the present limited accuracy of the data used in the calculations.

The reviewer is not able to deal with the chapters on the hydrosphere, atmosphere and the so-called biosphere so critically as with that on the lithosphere. There is here much intriguing information reasonably well documented. It is interesting to see how often the characteristic geochemical line of attack has been used of comparing the rates at which a geological process is adding or subtracting a particular element from one or other of the major geochemical units of the Earth with the amount actually found in those various units. Often the facts when found show discrepancies which sets the geochemist looking for a leakage from, or an addition to the supposed closed system; if no explanation of the discrepancies is found a new estimate of the rate of the process has to be made. An instance from among many of this line of approach is the case of bromine; the amount of this element taken to the sea by rivers is apparently not enough to account for the bromine content of the ocean and this suggests either an initial bromine content of the primordial ocean or considerable direct additions from volcanic sources. In these chapters there is often a wealth of factual information, as for example on the role of bacteria in geological processes, or the chemical changes involved in the production of coal and petroleum, but it is very clear that many of these topics have not yet received treatment by a master mind able to integrate the data into a general scheme.

Part II of the book, as already indicated, consists of separate chapters surveying the geochemistry of individual elements or of groups of related elements. In each case the authors deal, so far as data is available, with the following points:

1. The manner of occurrence of the element in the geochemical spheres of the Earth.
2. Its general geochemical character.
3. The manner of occurrence in mineral structures.
4. Its course during the normal crystallization of magmas (endogenic differentiation).
5. Its role in the processes of decomposition, transportation, and redeposition of matter during the cycle of weathering (exogenic differentiation).
6. Its abundance, particularly in the uppermost part of the silicate crust of the Earth.

In addition, the manner of occurrence and abundance of the element in meteorites is commonly discussed, and likewise its role, if any, in metamorphic phenomena and its concentration in mineral deposits of economic importance.

Compilations such as the various chapters of Part II of this work which give a summary of the available information on the distribution of the various elements in rocks and minerals, provide us with a fine opportunity of seeing the gaps in our knowledge. The data for the rocks are available only for very wide groups and much new data will be required to enable us to give the average values for more limited natural groups among the rocks. For many purposes, for instance, granite is far too comprehensive a rock group and the minor elements should be investigated in the various subgroups of the granites. When this is done perhaps the results will be more understandable than at present and there is no doubt that the data will then also play an important role in the development of petrogenetic theories. The question of the regional variation of elements in the lithosphere, as for example, the

variation of Be, Ti, Sr and Ba, is another line which cannot be effectively followed until data from more narrowly limited groups of rocks is available. In this second part of the book it is also very clear that explanations of the facts of the distribution of the elements resulting from the too enthusiastic use of GOLDSCHMIDT's ideas on the effect of ionic size and charge etc. have frequently been given by various workers and it will be necessary to review these more critically. The second part of this book should indeed give a great stimulus to geochemists first to reduce the gaps in our knowledge and secondly to tidy up our interpretation of the data.

The user of this monumental work by Professors RANKAMA and SAHAMA will inevitably feel profoundly grateful to them for providing so large a part of the data of the subject in this accessible form and for steering, on the whole, so well balanced a course through all the tentative hypotheses which necessarily exist in the present stage of the science. He will also not fail to realize how great a debt the science owes to F. W. CLARKE and V. M. GOLDSCHMIDT; these two will for ever remain great names in the science of geochemistry.

L. R. WAGER

HUTCHINSON, G. E.; **The Biogeochemistry of Vertebrate Excretion. Survey of Contemporary Knowledge of Biogeochemistry.** Nr. 3. Bulletin of the American Museum of Natural History, Vol. 96. New York 1950. 554 S. Preis 8/6.

Dies ist der dritte Band einer Serie, die der Darstellung unserer Kenntnisse auf dem Gebiet der Biogeochemie gewidmet ist. Im vorliegenden Teil wird sehr ausführlich die Biochemie der Guanoablagerungen besprochen, und zwar sind etwa $^3/_4$ des Textes der Beschreibung von Vogelguanolagerstätten gewidmet. Eine zusammenfassende Darstellung der Entstehungsbedingungen für diese Guanobildungen ist angeschlossen. Es folgt dann die Beschreibung der Höhlenguanolagerstätten mit einer kurzen Zusammenfassung. Eine vergleichende Geochemie der Guanominerale mit einer Zusammenfassung der neuen Ergebnisse beschließt den Text, dem eine ausführliche Bibliographie von 37 Seiten und ein Index folgen. Auf 16 Tafeln sind Bilder von Vogelkolonien, von Guanoinseln und Profilen durch Guanoablagerungen etc. gegeben.

Das Buch enthält eine Fülle von geochemisch wichtigen Tatsachen und Schlüssen, auf die im einzelnen nicht eingegangen werden kann. Es mag nur erwähnt werden, daß die von den Seevögeln aus dem Ozean an Land gebrachte Menge Phosphor von der Größenordnung $10^4$—$10^5$ t/Jahr ist, während die durch chemische Erosion dem Ozean zugeführte Menge Phosphor auf $10^7$ t/Jahr geschätzt wird. Jeder, der sich mit der Geochemie des Phosphors und der des Stickstoffs befaßt, wird das Werk zu Rate ziehen müssen. Aber auch über viele andere Elemente findet man interessante Angaben, wenn auch manche älteren Analysen wohl einer Nachprüfung bedürfen.

Das Buch ist ein schönes Zeugnis für die fruchtbare Zusammenarbeit zwischen Biologie und Geochemie.

C. W. CORRENS.

**Gmelins Handbuch der anorganischen Chemie,** 8. Aufl., System-Nr. 3 **Sauerstoff**, Lieferung 2: Vorkommen — Technologie. Hrsg. vom Gmelin-Institut in Clausthal-Zellerfeld 1952. Verlag Chemie G. m. b. H., Weinheim a. d. Bergstraße. 65,— DM.

Die vorliegende Lieferung der 8. Auflage des Handbuchs der anorganischen Chemie von GMELIN ist insofern für die Leser dieser Zeitschrift von Interesse, als das Vorkommen von Sauerstoff und Ozon auf 45 und das von Wasser auf 54 engbedruckten Seiten aufgeführt ist. Die Geochemie des Sauerstoffs und Ozons ist in durchaus selbständiger Form behandelt. Es wird das außerirdische Vorkommen des Sauerstoffs, der freie Sauerstoff in der Atmosphäre, im Meer, in Seen und auch der gebundene Sauerstoff in der festen Erdrinde unter Einschluß des Oxydationsgrades der Gesteine und der Bindung freien Sauerstoffs bei der Verwitterung besprochen. Das Vorkommen des Wassers ist ähnlich eingeteilt und ausführlich dargestellt. Leider sind die Verfasser der einzelnen Abschnitte nicht angegeben, Referent weiß, daß der Abschnitt über das Vorkommen des Sauerstoffs von W. VON ENGELHARDT stammt.

Das Ganze ist ein recht nützliches und, soweit der Referent beurteilen kann, auch recht vollständiges Nachschlagewerk für die Literatur bis Ende 1949. Bei der Besprechung der Sauerstoffisotope fehlen deshalb die neuesten Arbeiten. Aus dem Aufsatz von SILVERMAN in dieser Zeitschrift, Band 2, S. 26—42, geht hervor, wieviel in der Zwischenzeit gerade auf diesem Gebiet gearbeitet worden ist.

C. W. CORRENS

Bijvoet, J. M., the late Kolkmeyer, N. H. and MacGillavry, Caroline H.; **X-Ray Analysis of Crystals.** Pp. xii + 304. London, Butterworths, 1951. 50 s.

This book can be thoroughly recommended to all students of X-ray crystallography and is particularly suitable for beginners. Nothing is taken for granted and all the techniques are carefully explained, step-by-step. A remarkable feature of the book is the wealth of truly excellent illustrations including a number of annoted X-ray photographs chosen to give added clarity to the discussion in the text of the methods of interpretation. The chapter on structure determination by Fourier methods is particularly well written and can be understood by even the mathematically ignorant reader. After an account of the principal methods of analysis, experimental and theoretical, the book goes on to describe a wide range of crystal structures. It therefore provides a useful summary of crystal chemistry in addition to its treatment of techniques. The main structure types are illustrated in many cases by photographs of models which give as good an idea as is possible on paper of the 3-dimensional reality. The discussion of mineral structures is extensive and clear and should prove useful to the student of mineralogy and petrology. A somewhat cumbersome feature of the book is the large number, 9 in all, of long appendices. These constitute about one-quarter of the book and while their separation is perhaps pedagogically justified, their existence shows how difficult it now is to review adequately the whole field of X-ray crystallography in one book of reasonable length. The subject has grown so enormously, and impinges on so many other sciences, that a comprehensive account of the whole field would be prohibitively long. On the whole, many more readers are interested in the presentation of the *results* of crystal analysis than require detailed guidance in the techniques.

The science of X-ray crystallography is somewhat overburdened with general treatments of the subject, all covering much the same ground, and it can be argued that a halt might conveniently now be called to the output of this sort of introductory text-book. This argument is certainly strengthened by the appearance of the English translation of Bijvoet, Kolkmeyer and MacGillavry which will serve for many years as a reliable guide to students and debutants in research. D. P. Riley

Shand, S. J.: **Eruptive rocks—their genesis, composition, classification, and their relation to ore-deposits;** with **a chapter on meteorites.** London: Thomas Murby & Co. 1950. 479 pp., illus., pls. 4th edition. 30 s.

Shand, S. J.; **The study of rocks.** London: Thomas Murby & Co. 1951. 217 pp., illus., appendix, 3rd edition. 12 s. 6 d.

These welcome new editions are both of books by Professor Shand which have already achieved a considerable success, the first presenting a rational system of petrology, the second a student's introduction to rocks from the field and petrographical points of view. Since its first appearance in 1927, the "Eruptive Rocks" has found wide acceptance as a standard textbook of advanced petrology. It is written strictly from the point of view of a believer in magmas, both at the surface and in depth, but it is important to realise that Professor Shand does not imply that primary magma is necessarily a homogeneous liquid. In a footnote (p. 4) he says "rock-magma is the partly or wholly liquid material from which eruptive rocks are formed;" and he adds "there is no evidence that deep-seated rock magma was ever hot enough to be completely liquid." In the light of current fashions in petrology, some readers will certainly notice that no attention is paid to the possible origin of magmas, and, apart from late-magmatic and post-magmatic reactions, little to metasomatic effects; but this book still gives an admirable account of the evolution of eruptive rocks once a liquid or partly liquid melt is available. The fixed constituents, the constituent minerals of the eruptive rocks, are described, and the evidence is given for supposing that water and other "fugitive" constituents have played their parts. A most useful summary of the results of investigations of the physical chemistry of artificial silicate melts leads on to a discussion of the freezing of the magma and the concentration of residual fluids. A series of important eruptive rock complexes are then described to illustrate the possible causes of heterogeneity in such rocks.

It was one of the author's intentions in the original edition to bring theory and practice together by indicating the link between eruptive rocks and ore deposits. The chapter dealing with ore-deposition was omitted from the second edition, but a revised section was introduced into the third edition, of which the present edition is a reprint. A direct connection between residual solutions from granite and the "oxidic" (tin-tungsten and lithium-beryllium-tantalum) deposits is traced via the pegmatites, but when he deals with the sulphide ores, Professor Shand finds that many of the claims that have been made about their magmatic origin must be held to lack adequate backing. While all investigators of ore-genesis will support his plea for experimental work on the behaviour of sulphides in silicate melts,

few will admit that it is necessary to adopt as agnostic a position as his, particularly when the clear field evidence of a direct connection between the "oxidic" and the sulphide ores, such as is shown in the Cornwall-Devon mineral field, is considered.

The remainder of the book is devoted to an exposition of Professor SHAND's classification of eruptive rocks, based on the "saturation" principle.

The stress laid on the chemical aspects of petrology in the "Eruptive Rocks" makes the book of interest to all students of geochemistry. The author remarks "Petrology needs all the help that chemistry can give it; but before they look for help, petrographers must learn to express their problems in terms that a chemist can understand." This book goes far towards showing them how to achieve this object.

"The Study of Rocks" deals with the metamorphic and sedimentary rocks as well as with the eruptive class. It gives an adequate account of the field appearance and mineralogical and chemical characteristics of the principal rocks, and it may be recommended as a useful book for students who have already obtained a good grounding in the principles of geology. There is an appendix on the chemical analysis of rocks.

K. C. DUNHAM

# Report of the President of the Commission of the Geochemical Localization of the Elements

The first two meetings of the commission were held at the Hotel New Yorker, September 5–6, 1951.

The following members had been appointed provisionally by the Executive Committee of the International Union of Pure and Applied Chemistry:

P. NIGGLI, President, Zurich
M. FLEISCHER, Washington
E. RAGUIN, Paris
T. F. W. BARTH, Secretary, Oslo
D. GUIMARAES, Belo Horizonte
A. HOLMES, Edinburgh.

The last two were not present, but submitted written opinions.

The meeting was called to order by Prof. NIGGLI.

1. The provisional constitution was confirmed, with P. NIGGLI as President and T. F. W. BARTH as Secretary.

2. It was agreed that the great importance of geo-chemistry, especially in nuclear studies, in mining and metallurgy, in agriculture and other fields of pure and applied chemistry, justifies the establishment of a commission and possibly later a section of geochemistry within the Union.

It was also agreed that it is impossible to localize the chemical elements without discussing the geological milieu.

Despite the large volume of work being published in the field of geochemistry there is scarcely any phase of research in this field that does not now suffer from a lack of accurate determinations made on well-chosen, representative, and adequately described materials. Too often, precise chemical and physical measurements that have been made on rocks, ores and minerals are not useful because the material has either not been characterized sufficiently or is not representative.

It is therefore urged that samples collected for chemical study be chosen, whenever possible, in consultation with geologists familiar with the region and chemists familiar with the problems. Rocks, ores, and minerals selected for study should be properly characterized. For rocks, data on the extent of the formation or body that the sample represents is indispensable, as is the petrographic determination of the mode, *i.e.* what minerals are present and in what proportions, and also information as to the variability within the unit sampled. Similarly, the value of chemical studies of minerals is greatly enhanced if optical and physical data are also made on the same sample, any variability noted, and the paragenetic relations to the associated minerals are stated.

It is highly desirable, when chemical studies have been made that representative material be set aside so that additional data can be obtained in the future.

3. The commission will not now attempt to define accurately its sphere of activity, but, with experience, the relations to other groups (International Geological Congress, International Geophysical Union, etc.) will be established in order to secure cooperation and to avoid duplication of work.

4. a) The commission will act as a clearing house, with one office in Washington, D.C. (headed by Dr. FLEISCHER), another in Oslo, Norway (headed by Dr. BARTH), for information pertaining to the various kinds of geochemical activities now in progress all over the world. Approximately 1000 geochemists will be circularized to obtain this information.

b) The commission will encourage work in geochemistry and try to organize symposia and encourage the preparation of monographs and bibliographies on the various chemical elements. Furthermore, the commission is particularly interested in the revision of CLARKE's "Data of Geochemistry", as well as in compilation of analyses of rocks, minerals, and natural waters on a regional and on a world-wide basis.

5. The Commission expects to publish a report each year. It is hoped to find an arrangement by which "Geochimica et Cosmochimica Acta" will print the annual reports, and also possibly other publications and announcements prepared by the Commission*.

* The Editors of Geochimica et Cosmochimica Acta have gladly agreed to publish the annual reports and, from time to time, other announcements.

## Announcement to Geochemists

At the recent meeting of the International Union of Pure and Applied Chemistry in New York and Washington, the Commission on Geochemical Localization of the Elements, organized by the Section of Inorganic Chemistry, held its first meetings (see the previous report). It was agreed that one of the needs of the field that could be met by the Commission, was to act as a central source of information as to what research in geochemistry was being undertaken and where. It is therefore requested that persons and organizations that now have under way, or that expect in the near future to undertake research projects or bibliographic projects in the field of geochemistry should inform the Commission of these projects and their scope. Those in the Western Hemisphere should write to Dr. MICHAEL FLEISCHER, U.S. Geological Survey, Washington 25, D.C.; those elsewhere should write to Prof. T. F. W. BARTH, Geological Museum, Oslo 45, Norway.

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